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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

RUBBER DIVISION ACTIVITIES

THE RUBBER DIVISION OF THE AMERICAN CHEMICAL SOCIETY

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Sergeant-at-Arms...E. H. KRISMANN

"MINUTES" OF THE MILWAUKEE MEETING AND ELECTION OF OFFICERS

The meeting of The Rubber Division, scheduled for the Convention of the American Chemical Society in Milwaukee, September 5 to 9, 1938, was cancelled by the Executive Committee because only three papers were submitted. This paucity of papers was the result of American rubber chemists and technologists giving wholehearted support to the International Rubber Technology Conference in London last May by contributing twenty-one papers.

ELECTION OF OFFICERS

The volume of work devolving on the Secretary-Treasurer had been increasing steadily for several years; therefore the 1937-8 Executive Committee, at the suggestion of C. W. Christensen, voted to divide the duties of the Secretary and Treasurer. The Chairman, A. R. Kemp, appointed H. I. Cramer to serve as Secretary until the next election.

In consequence of the cancellation of the meeting at Milwaukee, the election of officers for 1938-9 was conducted by letter ballot. From a slate of nominees presented by a nominating committee, composed of H. L. Fisher, chairman, Bruce Silver and J. H. Ingmanson, the following officers were elected for the coming year:

Chairman....................G. K. HINSHAW, Goodyear Tire and Rubber Co.
Vice-Chairman............................E. B. CURTIS, R. T. Vanderbilt Co.
Secretary...............................H. I. CRAMER, University of Akron
Treasurer.......................C. W. CHRISTENSEN, Monsanto Chemical Co.
Sergeant-at-arms..........E. H. KRISMANN, E. I. du Pont de Nemours and Co.
Executive Committee...................A. R. KEMP, *ex-officio,* J. C. WALTON, A. W. CARPENTER, G. S. HASLAM, W. G. NELSON

H. I. CRAMER, *Secretary*

THE MEETING OF THE RUBBER DIVISION IN BALTIMORE, MARYLAND, APRIL 4-5, 1939

The meeting was held in the main Ballroom of the Emerson Hotel, with approximately three hundred and fifty in attendance.

On April 4, a Symposium on Synthetic Rubber and Elastic Polymers comprised the following papers:

1. Plasticization of Neoprene Type G. By H. W. Starkweather and M. A. Youker.
2. The Effect of Pigmentation on Neoprene Type G. By N. L. Catton and D. F. Fraser.
3. The Effect of Various Modifying Agents on Neoprene Type G. By M. F. Torrence and D. F. Fraser.
4. Neoprene Cements. By H. W. Starkweather and F. C. Wagner.
5. Adhesion of Neoprene to Metal. By F. L. Yerzley.
6. The Buna Rubbers. By Albert Koch.
7. The Nomenclature of Synthetic Rubbers. By H. L. Fisher.
8. Chemical and Physical Research in the Field of Polymerization. By S. D. Gehman, H. J. Osterhof, and L. B. Sebrell.
9. Recent Developments with Koroseal. By F. K. Schoenfeld, A. W. Browne, Jr., and S. L. Brous.
10. Vapor Pressures and Accommodation Coefficients of Four Non-Volatile Compounds. The Vapor Pressure of Tri-*m*-Cresyl Phosphate over Polyvinyl Plastics. By F. H. Verhoek and A. L. Marshall.
11. A Comparison of the Commercial Polysulfide Rubbers. By S. M. Martin, Jr.
12. Plastics in the Cable Industry. By R. A. Schatzel and G. W. Cassell.

The second day was devoted to general papers:

1. The Variability of Plantation Latex. I. Surface Tension. By D. S. Villars.
2. Hevea Latex of Large Particle Size. By J. McGavack.
3. A Method of Determining the Distribution of Flock Size in the Creaming of Hevea Latex. By E. M. McColm.
4. Sol and Gel in Hevea Latex and Crude Rubber. Influence of Oxidation on Gel-Sol Transformation. By A. R. Kemp and H. Peters.
5. The Colloidal Structure of Rubber in Solution—Colloidal Aspects of Vulcanization. By S. D. Gehman and J. E. Field.
6. Refractometer Studies on Rubber-Pigment Mixtures. By H. C. Jones.
7. The Composite Nature of the Stress-Strain Curve of Rubber. By I. Williams and B. M. Sturgis.
8. Continuous Vulcanization of Belting. By J. M. Bierer and T. M. Knowland.
9. The Surface Chemistry of Rubber Carbon Blacks. By A. W. Campbell.
10. Nitroparaffins and Chloronitroparaffins as Inhibitors of Gelling in Vulcanizing Cements. By A. W. Campbell.

On Tuesday evening, three hundred and twenty-five members and guests attended the Divisional banquet held in the main Ballroom of the Hotel Emerson. Following a dinner program of music, J. M. Bierer reported on plans for the Boston meeting. General Hugh Johnson gave an address on Current Events in his stimulating manner and responded to questions until a late hour. The Division is indebted to V. L. Smithers and his committee, Enos Baker, C. A. Bartle and S. G. Byam, for the unusually fine dinner and excellent program.

At the conclusion of the papers on April 5, a general business session was held. R. H. Gerke, Chairman of the Crude Rubber Committee, reported on the ac-

tivities of this committee for the past year. A vote of thanks was extended the committee for its fine work. It was also voted that the committee continue with its present personnel for the coming year. W. S. Davey of England discussed the report of the Crude Rubber Committee and expressed the appreciation of the British Rubber Growers of the efforts and progress of the committee in evolving specifications for crude rubber.

The Rubber Division was glad to welcome Mr. Davey at the meeting. Mr. Davey was on his way to the Far East, where he will be Head of the Chemical Division of the Rubber Research Institute, Malaya, a position which Dr. E. Rhodes recently resigned.

It was voted that a committee be appointed by the Chairman to review H. L. Fisher's paper on the Nomenclature of Synthetic Rubbers and make recommendations relative to this question to the Division at its next meeting.

H. E. Howe, Editor of *Industrial and Engineering Chemistry,* spoke briefly on the plans for the Boston meeting, where the general meeting and the general banquet of the Society will be under the sponsorship of the Rubber Division. He expressed the hope that all papers on vulcanization will be submitted early enough for publication in the October issue of *Industrial and Engineering Chemistry*.

The Chairman, G. K. Hinshaw, urged members of the Division to give their fullest support to the Boston meeting, and stressed the unusual responsibilities of the Division at that time. He assured the membership that their suggestions for running the Division would be welcomed at all times. In conclusion he requested that authors make every effort to improve the quality of slides and presentation of papers.

The following secretary's report was written into the record:

Total membership to date, March 31, 1939		573
Members paid for 1939	462	
Associate Members paid for 1939	111	
New Members and Associate Members for 1939 (included in above figure)		68
Regular Members	43	
Associate Members	25	
Total membership not paid for 1939		44
Regular Members	25	
Associate Members	19	
Subscriptions paid for 1939		186
Subscriptions not renewed for 1939		37
Honorary Members and Exchange		38

H. I. Cramer, *Secretary*

NEW BOOKS AND OTHER PUBLICATIONS

Charles Goodyear—An Intimate Biographical Sketch. By Hugh Allen. Goodyear Tire & Rubber Co., Akron, Ohio. 6½ x 8½ in. 16 pp.

As indicated by the sub-title, this booklet sketches the life and work of Charles Goodyear, the discoverer of vulcanization. It traces his ancestry, early struggles, the discovery of vulcanization, the legal battle with Horace H. Day, Goodyear's later work, and finally his death. A chronology is included. The booklet is illustrated with drawings depicting highlights in the inventor's career. [From *The Rubber Age* of New York.]

Rubber and the Goodyear Plantations. By Hugh Allen. Goodyear Tire & Rubber Co., Akron, Ohio. 7 x 10 in. 32 pp.

After briefly tracing the development of rubber cultivation from its early "wild" stage to the scientific plantation stage, this booklet tells how and why Goodyear entered the field of rubber production, and describes its three company-owned plantations in Sumatra. The building-up of these plantations, from the clearance to the actual productive state, is told in words and pictures. The booklet also touches on some of the factors which have and are affecting the rubber industry at large, such as the Stevenson Plan and the current restriction scheme. [From *The Rubber Age* of New York.]

Uses and Possibilities of Rubber in Agriculture. By Alexander Hay. British Rubber Publicity Association, 19 Fenchurch St., London, E.C. 3, England. 5½ x 8½ in. 28 pp.

This bulletin, the eighth in the "Rubber and Agriculture" series sponsored by the British Rubber Publicity Association, affiliated with the International Rubber Regulation Committee, is a reprint of the paper presented by Mr. Hay at the Rubber Technology Conference held in London last May. The various uses of rubber on the farm and in the dairy are briefly described, with many being illustrated. A bibliography is included. [From *The Rubber Age* of New York.]

Index to A.S.T.M. Standards and Tentative Standards. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 6 x 9 in. 140 pp.

This latest edition to the A.S.T.M. standards and tentative standards gives information on all of the 870 standards as of January 1, 1939. It is of service to anyone wishing to ascertain whether the Society has issued standard specifications, test methods, or definitions covering a particular engineering material or subject, and is of help in locating the standards in the volumes where they appear. All items are listed in the Index under appropriate key-words, according to the particular subjects they cover. [From *The Rubber Age* of New York.]

The Chemical Formulary. (Vol. IV.) Edited by H .Bennett. Published by Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St., New York City. 5½ x 8½ in. 632 pp. $6.00

New and additional formulas gathered since publication of the third volume of this book accumulated in such a quantity as to warrant the issuance of this,

the fourth volume. Not only does this latest edition incorporate hundreds of additional formulas, but because many purchasers of the book are beginners in the art of chemical compounding an explanatory introductory chapter has been included. This chapter explains the purpose of the "Formulary" and gives complete directions for making simple preparations which are in everyday use. Like previous editions, the book is both a time and work saver for technical workers, instructors and chemists. It includes formulas for a number of latex and rubber products. [From *The Rubber Age* of New York.]

THE ECONOMICS OF CHEMICAL INDUSTRIES. By Edward H. Hempel. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York City. 6 x 9 in. 260 pp. $3.00.

The characteristic background and the economics common to the American chemical industries are given in this book. The author defines a chemical industry as "any industry which transforms the matter contained in raw materials or crudes into chemicals of a higher order better suited for further purposes." Following this definition, he includes the rubber industry, although he states, that this industry, like several others, has grown to such great size that it is given status as a separate industry and in this country is no longer considered within the chemical group. The book consists of 11 chapters, an appendix, bibliography and index. The history, scope, patent situation, price structure, and economic requirements of various light and heavy chemicals are covered. There are numerous tables and several inserts. [From *The Rubber Age* of New York.]

PHYSICAL CONSTANTS OF HYDROCARBONS. Volume I. A.C.S. Monograph 78. By Gustav Egloff. New York, Reinhold Publishing Corp. 403 pp. $9.00.

This is the first of a series of four volumes by Dr. Egloff, presenting in tabular form complete data on the most important physical constants of hydrocarbons. Volume I covers paraffins, olefins, acetylenes and other alipathic compounds; Volume II, to be published in the fall, will deal with cycloparaffins and cycloolefins; Volume III will contain the aromatic series; Volume IV will correlate the physical properties of all groups with their structure.

The body of the book contains no text. For each hydrocarbon are given in parallel columns its carbon skeleton, melting point, boiling point and index of refraction, with additional data when available.

One of its excellent features is the inclusion of data on the less-investigated higher members of different homologous series, *e. g.*, heptahexacontaine and 3,12-diethyltetradecadiene-2,12. A glance through the pages reveals the extensive work done on some compounds and the neglect of many others which may become equally important. The author is to be congratulated on a necessary piece of work, well done.

CASEIN AND ITS INDUSTRIAL APPLICATIONS. A.C.S. Monograph 30, Revised Edition. By Sutermeister and Browne. New York, Reinhold Publishing Corp. 433 pp. $6.50.

An extremely interesting and readable volume, discussing thoroughly important phases of casein, including its organic and physical chemistry, manufacture and storage, together with such industrial applications of this versatile substance as glue, paint, food products, plastics, synthetic wool fiber and paper coating. Mention is also made of patents for casein as an ingredient of latex and of hard rubber. This book will well repay reading by those who wish to keep in touch with the latest developments in protein chemistry, as well as with recent notable advances in the practical utilization of casein.

SOLUBLE AND INSOLUBLE RUBBER *[1]

H. STAUDINGER

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A particularly striking property of unvulcanized rubber is that benzene-soluble rubber, which is a colloid capable of unlimited swelling, is transformed on standing into insoluble rubber—a colloid of limited swelling capacity. Scarcely any difference in composition can be found analytically between the two kinds of rubber, which differ so widely in solubility. Insoluble rubber can be reconverted into a soluble form by long standing or by mastication. These apparently reversible transformations[2] between soluble and insoluble rubber were formerly ascribed to a micellar structure of rubber; it was assumed that the swelling phenomena, as also the high viscosity of rubber solutions, were connected with the solvation of the micelles. In contrast to such micellar theories it was shown, by the conversion of polymer-homologous rubbers into the polymer-analogous hydrorubbers[3], that the colloidal particles in dilute solutions are the macromolecules themselves. The high viscosity of rubber solutions is caused by the thread-like form of the macromolecules and not by a micellar structure[4]; rubber thus belongs to the linear molecular colloids.

On the basis of our knowledge of the size and form of the rubber molecule the apparently reversible transition of soluble into insoluble rubber can be explained in the following manner: the long thread-molecules of the rubber become linked together by a few bridges into three-dimensional macromolecules during transition from soluble to insoluble rubber. Such a union of two thread-molecules occurs only through oxygen atoms. This can be shown by the fact that specimens of pure rubber, prepared with careful exclusion of air, remain soluble and do not change during long standing if air and light are excluded. If on the other hand a small amount of air is admitted, rubber is slowly converted into the insoluble form; that is, it is transformed into a product which, although it swells strongly, does not pass into solution. Finally, if atmospheric oxygen acts for a long time on rubber, the insoluble material is again converted into a soluble form. The three-dimensional macromolecules of the former are formed of long thread-molecules joined together by a few oxygen bridges; by oxidation the macromolecules are broken down into short pieces, which may be branched but yet are soluble. Thus a low-molecular soluble rubber is produced. Transformation of insoluble into soluble rubber is therefore not a reversible process; soluble rubber produced from the insoluble form is no longer identical with the original material but is a product strongly degraded by oxidation.

Owing to the length of the thread-molecules of natural rubber[5], which possess a degree of polymerization of 2,000, extraordinarily small amounts of oxygen suffice to bring about the linking of the thread-molecules into three-dimensional macromolecules. In the most favorable case two oxygen atoms are sufficient (an assumption that is never completely realized in practice); thus, 32 grams of oxygen could transform 136 kilograms of soluble rubber into the insoluble form, provided these oxygen atoms formed bridges between all the thread-molecules.

Further experiments showed that even with scrupulous exclusion of oxygen, soluble rubber can be rendered insoluble merely by the action of light. It must

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 98, pages 253-254.

therefore be possible for a direct linking of the thread-molecules into three-dimensional macromolecules to take place. This arises by the double bonds of one thread-molecule reacting with those of another. That a linking of separate thread-molecules into even longer thread-molecules can take place is shown by the observation that the viscosity of a solution of a rubber that has been exposed to light, with scrupulous exclusion of air, increases; for example, the specific viscosity of a 0.1 molar solution, *i. e.*, one containing 0.68 gram rubber in 100 cc. tetralin, increased from 8.8 to 12.0 after the rubber had been kept in nitrogen in daylight for 12 weeks. During storage in the dark, on the other hand, the rubber did not change, and the specific viscosity of its solution remained completely unaltered. On standing in light for about six months with exclusion of air, this rubber was largely converted into the insoluble form; the small residual soluble fractions gave highly viscous solutions. When, on the other hand, rubber was exposed to air it was again partly converted into insoluble rubber, but the soluble fractions gave low-viscosity solutions, as they consisted of strongly degraded rubber.

From these experiments it follows that the sensitive rubber molecule remains unchanged only on keeping with the most scrupulous exclusion of air and light, and that, on the other hand, by admission of air or exposure to light, relatively small chemical changes take place in the macromolecule which, however, result in profound physical changes in the rubber.

Similar profound changes in physical properties by traces of foreign substances have been observed also with polystyrene, for instance. By polymerization of pure styrene there is obtained a soluble polystyrene capable of unlimited swelling, and which consists of thread-molecules. By adding small amounts of divinylbenzene (0.01%) to monomeric styrene, however, there is formed after polymerization an insoluble polystyrene that swells only to a limited extent, because its thread-molecules are linked together into three-dimensional macromolecules by divinylbenzene bridges[6].

REFERENCES

[1] 48th Communication on Isoprene and Rubber. The 47th Communication by Staudinger and Mojen appeared in *Kautschuk* **13**, 39 (1937).
[2] Bary and Hauser, *Kautschuk* **4**, 97 (1928).
[3] Staudinger and Leupold, *Ber.* **67**, 304 (1934).
[4] Staudinger, "Die Hochmolekularen Organischen Verbindugen Kautschuk und Cellulose," Berlin **1932**.
[5] Staudinger, *Ber.* **68**, 1682 (1935).
[6] Staudinger and Heuer, *Ber.* **67**, 1164 (1934); Staudinger and Huseman, *Ber.* **68**, 1618 (1935); Staudinger, Heuer and Huseman, *Trans. Faraday Soc.* **32**, 323 (1936).

STRUCTURE OF RUBBER *

C. J. B. CLEWS

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INTRODUCTION

X-ray methods have had so many triumphs in the elucidation of the fine structure of crystalline substances that it is not surprising that they were applied to the problem of the structure of amorphous substances. Katz[1] showed that unstretched rubber gave an x-ray diagram of two diffuse rings, which indicated that the rubber was in the amorphous state, but that on extreme stretching a fibre diagram was obtained which bore a striking similarity to the type of diagram produced in the single crystal rotation method. Since this early work the subject has been studied extensively, but the structure has still not been established beyond all doubt and, more particularly, little is known of the mechanism of stretching. It is proposed in this account to discuss the present position of our knowledge.

CRYSTAL STRUCTURE OF RUBBER

The earliest attempt to deduce an elementary cell from the x-ray fibre diagram was made by Hauser and Mark[2], and two years later Mark and von Susich[3] made a more precise investigation which led to an elementary cell, which has been generally accepted until quite recently. Their unit cell is orthorhombic with the dimensions: $a=12.3\pm0.1$, $b=8.1\pm0.1$, $c=8.3\pm0.1$ Å. The cell volume is 830 Å^3, and combining this with the measured density, 0.955, the number of isoprene residues in the unit cell is found to be 7.1 ± 0.3 This is incompatible with the orthorhombic crystal class. The error is probably due to the uncertainty of the density measurements, and Mark and von Susich suggest that the number should be 8. An interesting feature of their work was the observation that thin films showed "higher orientation" to x-rays on stretching, *i. e.*, there were characteristic differences in the intensities of the x-ray reflections when two photographs were taken, one with the radiation perpendicular to the plane of the film and the other with the radiation parallel to the plane of the film. This phenomenon will be discussed in more detail later. The long polymerized isoprene chains (*Hauptvalenzketten*), of which rubber undoubtedly consists, lie parallel to the direction of stretching, four such chains running through each cell. The chains are probably in the *cis* form[4].

The next important contribution was contained in a paper by Lotmar and Meyer[5], who undertook the investigation in view of the great improvement in x-ray technique and of the increased knowledge of the atomic distances and valence angles of organic substances. The period of the fibre axis computed from the layer-line separation is 8.20 ± 0.05 Å, while the spacings calculated from the first two equatorial reflections are 8.47 ± 0.05 and 12.57 ± 0.05 Å. Owing to the difficulty of indexing several reflections in the orthorhombic lattice, they were led to deduce the monoclinic cell: $a=8.54\pm0.05$, $b=8.20\pm0.05$, $c=12.65\pm0.05$ Å, $\beta=83°20'$. The angle, chosen by the graphical method of Sauter, permits the assignment of the indices (304) to the equatorial reflection A_4. The highest value for the density of stretched, crystalline rubber recorded in the literature

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 34, pages 955-960.

is 0.965, which gives 7.6 for the number of isoprene residues in a unit cell. This value is nearer to 8 than the previous one, but the deviation is still extraordinarily large. It is interesting to note that the same anomaly occurs with the inorganic "rubber," polyphosphornitrile chloride[6], which suggests that it depends on the peculiar physical properties of these substances and on the open texture of the very small crystallites. The essential correctness of the x-ray density of 1.02 for rubber, in comparison with 0.94 for amorphous rubber, is supported by the fact that other hydrocarbons, namely the paraffins, have a density difference of approximately 10% between the solid crystalline and the liquid amorphous states. From a consideration of reflections and absences, Lotmar and Meyer deduce the space group as C_{2h}^5. An exact determination of all the parameters is not possible, owing to the relatively poor diagrams and to the large number of these parameters. The long chains are parallel to the fibre axis, but Mark and von Susich's supposition that the chains are planar is no longer tenable, because with such a structure a single C_5H_8 residue has a length greater than one-half the fibre period, unless the valence angles are made smaller than those generally accepted.

Employing a new method, Sauter[7] finds an orthorhombic cell: $a=12.60\pm0.05$, $b=8.20\pm0.05$, $c=8.91\pm0.05$ Å. There is a relatively large difference of 0.37 Å between the length of the c axis found by him and by Lotmar and Meyer, which is ascribed to the large experimental errors in the work of the latter. Sauter's data give 7.92 for the number of C_5H_8 residues per unit cell. His space group has been strongly criticized by Mark and Meyer[8] on the grounds that he has indexed some of his reflections incorrectly, owing to the use of specimens which were not highly orientated. There is a similar controversy between these workers over the structure of cellulose.

Morss[9] has proposed a monoclinic cell: $a=26.3\pm0.1$, $b=8.15\pm0.1$, $c=8.9\pm0.1$ Å, $\beta=109°5'$. Again the disparity in the length of the c axis will be noted, while the a axis is slightly greater than twice the length usually accepted. It is claimed, however, that this cell gives better agreement with experimental facts. No mention is made of Sauter's investigations.

In an attempt to decide between the somewhat conflicting evidence, the present author has made careful x-ray measurements which lead to spacings, calculated from the layer-line separation and the first two equatorial spots, of 8.12, 12.59, and 8.46 Å, respectively. If the monoclinic angle $\beta=83°20'$ is now introduced, the data are in excellent agreement with Meyer and Lotmar's figures, *viz.*, $a=8.52$, $b=8.12$, $c=12.68$ Å, and calculations of the other lattice spacings serve to confirm the correctness of their assignment of space group and unit cell. Further work is in progress in the hope of producing better photographs showing more reflections, and thereby opening up the possibility of applying the more exact methods of Fourier analysis to the data.

MICELLAR OR CRYSTALLITE STRUCTURE

A very important question that arises is how rubber, which in the unstretched state shows an amorphous ring diagram, gives a fibre diagram on stretching. Iguchi and Schossberger[10] have studied carefully the effect of different degrees of stretching on the x-ray diagram, and find that crystal interference becomes evident at extensions greater than 100%, and with increasing extension the intensities of the rings decrease while those of the crystalline reflections increase. This undoubtedly indicates a gradual internal change.

The micellar theory of fibre structure, originally developed for the cellulose structure, offers a qualitative explanation of the behavior of rubber. The older

theory considers the micelles as separate crystallites, between which lie the intermicellar spaces. The micelles consist of groups of long-chain molecules (*Hauptvalenzketten*) bound together along their length by homopolar bonds and in the transverse direction by van der Waals' forces, the intermicellar binding being also attributed to van der Waals' forces. The original model of Meyer depicts the micelles arranged like bricks in a wall, and doubtless this offers the simplest explanation of the x-ray results[4]. It is difficult, however, to understand how such an arrangement can give a micellar structure its peculiar mechanical properties. More recent theories[11,12,13] suppose that a given *Hauptvalenzkette* is not confined to a single crystalline region, but may stretch through several such regions. There is substantial experimental evidence for this idea. From measurements of the breadths of the interference patterns, Hengstenberg[14] estimates the dimensions of the micelles to be of the order $600 \times 500 \times 150$ Å, whereas molecular weight determinations indicate a chain length of the order 7000 Å.

Another phenomenon which has been observed with both rubber and cellulose is that of "higher orientation," by which is meant an ordering of the crystalline regions so that they are parallel, not only to the fibre axis, but also to a second crystallographic direction. In a fibre or in stretched rubber, the micelles lie with their long axes parallel to the fibre axis (b axis), while the a and c axes lie in quite different directions in different parts of the fibre, but with the appearance of higher orientation the direction of the *Hauptvalenzketten* remains as before, while a parallel ordering of the a and c axes occurs. Mark and Kratky[15] consider that sliding in the lattice or rotation of the single chains cannot give rise to this orientation, but that it is necessary to suppose the existence of lath-shaped micelles which possess, on account of their shape and of their transverse bindings, a definite individuality, even though the *Hauptvalenzketten* extend beyond the sphere of single micelles. It has been shown by Schossberger and Clews[16] that the property of building up these aggregates is not merely a characteristic of naturally occurring conditions, but is an intrinsic property of the *Hauptvalenzketten* themselves.

A number of ideas have been put forward to explain the amorphous diagram of rubber in the unstretched condition. One of the earliest and possibly the most feasible is that the crystallites are insufficiently orientated to give an x-ray diagram, but that the crystals which on stretching give crystal interference are preformed[2]. Another idea, which has received little support, is that the micelles are built up by the stretching process[17]. A not unreasonable concept proposed by Fikentscher and Mark[18] is that in the unstretched state the isoprene chains are coiled to form spirals which are extended into long chains on the application of tension. While this, taken in conjunction with the orientation process, offers a seemingly satisfactory picture of the extension phenomenon, it is certainly not above criticism.

Beyond the work of Meyer[6] on an inorganic rubber-like substance, there are very few x-ray data available for synthetic substances. The author is at present preparing to make a series of experiments on such products.

STRUCTURE OF BUTADIENE AND ITS DERIVATIVES AT LOW TEMPERATURE

Considerable interest attaches to a study of the structure of isoprene, chloroprene and butadiene as the hydrocarbons which on polymerization give natural and synthetic rubbers. These substances are in the gaseous or liquid state at normal temperatures, and as it is possible to make exact x-ray measurements only in the solid state, they have been examined at liquid-nitrogen or liquid-oxygen tem-

peratures in a Debye-Scherrer camera of radius 57 mm., employing a simple technique developed in the Davy-Faraday Laboratory[19]. The source of x-rays was a large 6 kw. tube fitted with a rotating copper anticathode, the tube current being about 100 ma.

Butadiene gives an extremely good x-ray spectrum with about 35 measurable lines. Although the photograph provides adequate data as to the crystal spacings, it was not possible to identify the diagram with that of any of the crystal classes of high symmetry. It is possible that the substance is a crystal of a class which does not permit of an analysis by the Debye-Scherrer method. The spacings calculated from the Bragg relation are shown in Table I.

Isoprene, which is of more direct interest in the rubber problem, never seems to crystallize sharply, but gives a glassy mass. This is in accordance with the facts quoted by Beilstein. It is, therefore, not surprising that only liquid rings

TABLE I

BUTADIENE. COPPER $K\alpha$ RADIATION

Line	Intensity	Angle θ	d in A	Line	Intensity	Angle θ	d in A
1	ww	—	1.42	18	ww	—	2.35
2	ww	—	1.49	19	www	—	2.42
3	www	—	1.54	20	www	—	2.49
4	www	—	1.57	21	w	—	2.57
5	www	—	1.70	22	mw	—	2.73
6	m	—	1.74_5	23	mw	—	2.78
7	mw	—	1.76_5	24	mw	—	2.88
8	w	—	1.86	25	mw	—	2.97
9	w	—	1.90	26	s	13.94	3.19
10	w	—	1.93	27	s	13.52	3.30
11	w	—	1.95	28	ss	12.84	3.47
12	www	—	1.99	29	ss	12.52	3.55
13	s	21.42	2.08	30	s	—	3.87
14	w	—	2.13	31	s	10.86	4.08
15	www	—	2.17	32	s	10.49	4.23
16	m	20.30	2.22	33	ms	9.49	4.67
17	ms	19.82	2.27	34	m	—	5.85

appear in the x-ray picture. The substance was also studied using a 35 kw. tube, but even long exposures with this intense beam failed to bring out any lines. A photometric trace of one of the films indicated intensity maxima corresponding to spacings of 8.6, 2.4 and 2.0 Å. There seems to be no correlation between these values and any found for amorphous rubber.

Chloroprene never gave diagrams showing more than three lines corresponding to spacings of 3.28, 2.57 and 2.32 Å, and two diffuse rings whose maxima correspond to spacings of 11.78 and 3.24 Å.

CONCLUSION

The results of the x-ray study of rubber structure may be summarized as follow:

(1) The unit cell is monoclinic, space group C_{2h}^5, $a=8.53\pm0.05$, $b=8.16\pm0.05$, $c=12.66\pm0.05$ Å, $\beta=83°20'$, with four isoprene chains in the *cis* modification passing through the cell, which contains 8 C_5H_8 residues.

(2) In the unstretched state there is a random distribution of ordered crystalline regions and disordered regions. On stretching, the crystalline regions become orientated in one or more crystallographic directions, thereby giving rise to the

x-ray fibre diagram. The crystalline regions may be identified with the micelles, which are groups of *Hauptvalenzketten* bound together by van der Waals' forces; a given *Hauptvalenzkette* is undoubtedly associated with more than one micelle. It is possible that the abnormal elastic properties are due to the chains becoming aligned parallel to the direction of stretching, and in addition there may be some extension of the chains themselves. Such an effect has been observed by Astbury in his work on keratin.

Some recent work on the structure of butadiene and its derivatives in the solid state is described, which, although offering no immediate solution of our problem, may prove of value when further accurate data are available, both for these compounds and for the corresponding rubbers.

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RUBBER ELASTICITY AND GAS ELASTICITY *

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I. INTRODUCTION

All substances which are composed of long mobile chains show one peculiar property, *highly reversible elasticity*. Even though the range of temperature of this property may be notably variable (in the case of polyvinyl alcohol and rubber at about room temperature, in the case of polystyrene, sulfur, or Thiokol only at a higher temperature) still it is to be noted that for rubber-like elasticity the presence of long flexible chains is an indispensable factor. Thus, typical rubber elasticity occurs in polyvinyl alcohol (Vinarol), polybutadiene (Buna), polymethylbutadiene (methyl rubber), polyacrylic ester and also in its mixed polymerisate with vinyl chloride. This type of elasticity occurs also in sinew fibrin and muscle fibrin, in polychlorobutadiene (Neoprene, Sovprene), in polyethylene sulfide (Thiokol, Baerite), polyphosphornitrile chloride and finally in vulcanized oils (factice) and also in elastic sulfur. In the cases so far examined (natural rubber, Buna, methyl rubber), it has been found that the coefficient of elasticity increases proportionally to the absolute temperature, and that during the stretching heat is evolved. This behavior is contrary to that of normal elastic materials, steel, quartz, glass, etc.

It is striking that the substances which have this property of highly reversible (rubber-like) stretching are widely different chemically. This tempts one to ascribe that property to the similarity of their construction. For example, all the substances mentioned consist of long chain-molecules, which display a high degree of internal mobility. The number of members in these chains varies from 10^2 to 10^4 and their mobility is due to the kind of linkage between the members, mostly simple C-C bonds.

II. STRETCHING OF NORMAL SUBSTANCES AND OF LONG-CHAIN SUBSTANCES

It is important to state that, in contrast to the above, substances which do not possess these two properties, or possess them only in a minor degree, never display a considerable range of reversible stretching. On the other hand, they are characterized by the normal elastic properties of crystalline or amorphous solids. They differ in the degree of elasticity and especially in their thermoelastic behavior quite considerably from the long-chain substances above-mentioned. As to the way in which the normal elastic properties of crystalline or amorphous substances arise, at least a qualitatively sufficient idea may be deduced. The individual particles—atoms, ions, or molecules—occur in positions of equilibrium, regularly arranged in crystals, but not so regularly arranged in amorphous solids, and make small, almost elastic vibrations about these positions of equilibrium. These vibrations are stronger at high than at low temperatures. If such a material be subjected to stress, then the individual particles are displaced a little from their posi-

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tions of rest and vibrate about new positions of equilibrium. Their distance apart is rather greater than formerly and the energy minimum rather higher. The increase in the distance apart includes the stretching caused by the stress, and the raising of the energy at the rest position shows that a certain quantity of energy is stored up in the specimen, *viz.*, the elastic stress.

If the crystal be released, the lattice points return to their original positions of equilibrium, giving up their energy, and the original condition is completely restored. From thermodynamics it follows that the material cools on rapid stretching and warms on rapid contraction; this has been found by experiment.

Entirely different relations are met with in the case of rubber-like stretching. In this case the range of elastic reversible lengthening may extend to several hundred per cent. The stress-strain curve usually starts as a straight line from the point of origin, but later it takes a more or less complicated course according to the conditions of the experiment, so that the modulus of elasticity does not remain constant during the stretching. The modulus of elasticity for the linear initial part of the curve is in the region between 10^5 and 10^7 dynes per sq. cm., and is considerably less than in the stretching of crystals. In the course of rapid stretching the substance becomes warm and it cools again on contracting. This point has been stressed by Hock in recent papers.

If x-rays be transmitted through a rubber strip during stretching, as was first done by Katz, a diffuse ring is formed in the unstretched condition, and this indicates the amorphous structure of the material. This continues with but slight alteration up to 115% to 300% elongation. After this, close to the ring, sharp and clear crystalline interferences appear. From this it may be concluded that small oriented regions are formed during stretching. These have been exactly examined by Hauser and Mark, Mark and von Susich, Lotmar and Meyer and recently in particular by Thiessen and his colleagues. This work has led to a suggested structural model for natural rubber. Other long-chain substances display a similar, though not so strongly marked behavior. The modulus of elasticity and the general course of the stretching curve depend in a high degree on the temperature and the degree of vulcanization. Vulcanized products have typical rubber elasticity only to a moderate degree, or not at all. If too many transverse linkages are formed by the sulfur bridges between the single mobile chains, the typical rubber elasticity disappears and the normal behavior of a crystalline solid (hard rubber) is approached. The modulus of elasticity calculated from the initial portion of the stretch curve increases with rising temperature. This has been particularly established by Meyer and Ornstein and their colleagues.

The enumeration of these properties shows that the molecular mechanism of rubber elasticity is clearly and fundamentally different from that of ordinary elasticity. One cannot go far wrong in ascribing rubber elasticity to the presence of long flexible chains. Several years ago Meyer, from the results of his experiments on the dependence of the modulus of elasticity of rubber on temperature, pointed out that this elasticity is a kinetic effect.

III. INTRAMOLECULAR STATISTICS OF AN ISOLATED CHAIN MOLECULE

To start at the very beginning, let us consider an isolated chain molecule, a hydrocarbon chain with no side-chains and n links, *i. e.*, $(n+1)$ C atoms:

$$CH_3.CH_2\underbrace{\ldots\ldots\ldots}_{n-3}CH_2.CH_3$$

n should in this case lie between 10^2 and 10^4. This model is much simpler than natural rubber, owing to the absence of lateral methyl groups. The next point is to

study in principle the behavior of such a chain. Later we must take into consideration that the free rotatability in the above chain is not really complete and that the several chains in a macroscopic piece must exert a mutual resistance.

According to the laws of stereochemistry the single members are 1.54 Å long. Let the angle between the valencies be α; this is about 109°. If we stretch the chain to its full extent, its length is given by:

$$L=(n-1)l\sin\frac{\alpha}{2}\ldots\ldots\ldots(1)$$

This maximum length can be attained only in one way, *viz.*, when all the linkages lie in one and the same plane, and form a zig-zag. Call this length $r_{max}=L$, which indicates the complete or maximum stretching of the chain.

If we wish to bring the ends of the chains to another distance from one another, *e. g.*, distance r, where r is less than r_{max}, this may be attained in many different ways. Because of the internal mobility of the chains, the separate members can be arranged in very many different ways to give a distance r between the two end C atoms. Suppose a large number, say 1000, of such chains are thrown at random on the ground, then measure the distance between the ends of each single chain and make a list of them. Then, on the basis of combinatorial analysis, it is very improbable that the maximum distance will be found, for it can occur only in one way. Any smaller distance is much more likely to occur, and so will be found more frequently. For each assumed distance r between the two ends of the chain there will be a fixed number of possibilities of occurrence, which may be named, according to Boltzmann, the "complexion" of r. To calculate this "complexion" as a function of r, several assumptions must be made concerning the structure of the chain and its mobility. Let l be the length of one member, n the number of members and α the angle between two consecutive members, and assume complete freedom of rotation. Then the probability that the ends of such a chain shall be at distance r apart is given by:

$$W\,(n,l,\alpha,r)r^2.\,dr=3.\,\frac{6}{r}\,\frac{1}{n^{3/2}.\,l_\alpha{}^2}.\,e^{3r^2/2nl_\alpha{}^2}.\,r^2.\,dr\ldots.(2)$$

n = number of members
l = individual length
α = valency angle

$$l_\alpha{}^2=l^2.\frac{1+\cos\alpha}{1-\cos\alpha}$$

r must, of course, always be less than r_{max}.

The considerations just stated lead to the assumption that a chain in thermodynamic equilibrium with its surroundings, which receives thermal impulses conveyed irregularly from all sides of itself, takes up that position which exhibits the greatest probability. This is merely the application of Boltzmann's results to one single-thread molecule, and there can be no objection to it, so long as there are enough really independent elements to which statistical treatment may be applied.

We will now, in the light of Boltzmann's rule, assign to an isolated main-valency chain an entropy:

$$S=k\log_e W\ldots\ldots\ldots\ldots(3)$$

and from this attempt to deduce its general behavior. First we find that such a chain can of itself pass only into a condition of greater entropy, *i. e.*, of greater probability, and that, for the production of an improbable condition, work must be done. If, therefore, we have a chain whose ends are r apart from one another

and we wish to stretch it to the maximum length L, then we must perform work A, which corresponds with the entropy difference $S_r - S_L$. The consequence of doing this work is that the chain grows warm on rapid stretching. This exactly corresponds with the rise in temperature of an ideal gas on adiabatic compression, in the course of which there is a loss of entropy because spaces which were formerly accessible to the gas are now barred to it. This diminishes the number of possibilities.

The pressure p of a gas is exerted by the irregular molecular motion which tends to make a greater volume accessible to the gas, and therefore to raise the number of possible arrangements, which means an increase in entropy. In the same way, the tension σ at the ends of a stretched main-valency chain is caused by irregular heat vibrations of the individual members, which tend to restore the shorter condition. Since this shorter condition has a greater number of possibilities of occurrence, it is more probable and corresponds with a higher entropy. It may now be understood why rubber-like substances warm on stretching and cool on contracting. This is completely analogous to the behavior of ideal gases, and contrary to normal crystal elasticity.

In the case of ideal gases, the internal energy U is independent of the volume. In the same way, in the case of rubber, an "ideal" region may be defined, within which the internal energy is independent of the stress. Experiment has shown that there is in fact only a very small dependence of internal energy on the length in the case of lightly vulcanized specimens at about 250% stretch. In the case of real gases and of rubber compounds, which do not belong to this special region, this behavior changes and, through intermolecular forces, there arises a dependence of the internal energy on the volume or on the degree of stretching.

IV. EQUATION OF STATE FOR IDEAL RUBBER

We now wish to propose and prove an *equation of state* for ideal rubber, analogous to that for the ideal gas. If one combines (2) with (3) one obtains:

$$\sigma = kT \cdot \frac{3}{nl^2} \cdot \frac{1+\cos\alpha}{1-\cos\alpha} \cdot dl \qquad (4)$$

From (4) it follows that the modulus of elasticity E of stretched rubber-like substances must increase in proportion to the absolute temperature. This has been recently established by different authors in a range from about $-50°$ C. to $+80°$ C. This is in complete agreement with the idea suggested here and by Meyer, but in complete contradiction to normal elastic behavior. The equation also brings out clearly the proportionality between stress and strain. This is well confirmed by experiment, at all events in the initial part of stretching. The suggestions made, and the relations developed from it, are only for this portion of the stretching.

The relation (4) indicates also a connection between the stress in the rubber and the number of thread molecules per cc. Therefore it permits the calculation of the weight of a single chain, just as the equation of state does that of a unit mass of an ideal gas. Kuhn worked out this calculation, and found a molecular weight between 20,000 and 100,000. This agrees well with the common conception of the magnitude of main-valency chains.

It is noteworthy that in the case of rubber there is one specific heat for constant stress, C_s, and another for constant length, C_l. In the same way a gas has one molar heat at constant volume, and another at constant pressure. It is well known that, in the case of an ideal gas, the difference between these two quantities is R

per mole. From the formula deduced above, the value of the difference between the two specific heats in the case of rubber may be readily calculated. It is clear from this relationship that the quantity k has a similar meaning to the gas constant for the ideal gas.

V. HIGHER DEGREES OF STRETCH; TRANSITION TO REAL RUBBER

With the help of the suggested explanation of rubber elasticity, the most important properties can be satisfactorily and uniformly explained. Still, it must not be concealed that there is a great gap between the formula deduced and actual fact, and the bridging of it offers very notable difficulties. The relation (4) applies only to the initial part of the stretching curve in that section within which σ and dl are directly proportional to one another. If it be desired to continue, it is necessary to build up the equation of state on the basis of that for an ideal rubber, just as van der Waals' equation is developed from the ideal gas equation.

It is to be noted that suitable corrections must be introduced, both for the single chains and also for the interaction of the chains on one another. So far we have considered only single chains, which certainly do not occur naturally, and it will be necessary to drop our assumptions one by one. Further, it is incorrect not to take into account the mutual interaction of the chains on one another. Hence, the steps to be taken to improve the suggested simplest model may be divided into two groups. (1) The pure statics of an isolated thread-molecule with respect to attracting and repelling forces between the single members of the chain must be worked out. (2) The reciprocal reactions between the single chains in the portion under examination must be expressed in a suitable way.

(1) It must be noted that, contrary to van der Waals' forces of attraction and repulsion between the particles of a single chain, which so far we have taken as statically equivalent, these in reality show energy differences, and so are not equivalent. Rather each microscopic possibility of a fixed chain condition, taking into consideration the mutual forces between the individual parts, should be provided with a weight factor of the form $e^{\epsilon i/kT}$, and the statistical examination completed taking all these weight factors into account. As in the case of an actual gas, this is a very difficult problem. In the above case it appears to be impossible. Hence, an attempt will be made to include the repulsion forces in a volume correction, and the attractive force in a pressure correction. For the first, ascribe to the part of the chain already present a tubular or ribbon volume of its own, entry into which is barred to the other chain members. It follows that the probable length of such a chain is greater than that given by equation 2. A more exact calculation would carry us too far at present. It has, in another place, been carried out at least approximately, and shows that with this correction a rather longer arrangement is obtained, which agrees with the available data. (2) In considering the mutual reactions between the single chains, particular importance attaches to the fact that rubber, during further stretching, shows arrangement phenomena which can be experimentally observed in the well-known crystalline interference of stretched specimens. Similar, but not so clear, indications of the formation of lattice regions have been pointed out by Brill in polybutadiene and by Carothers in Neoprene. These phenomena show that at large extensions the chains, which are already mostly in a stretched condition, gradually assume a micellar form under the influence of their mutual forces of attraction. These micelle-like structures can be observed in the interference image, and their magnitude has been approximately determined by Hengstenberg and Mark.

In the case of the relatively short chains of paraffin hydrocarbons, owing to the low number of members, the stretched or almost fully stretched form fitting into a crystal lattice is only slightly more improbable than the most probable resulting from the statistical law. The natural energy and entropy variations suffice, therefore, in such a system to produce stretched chains with sufficient frequency for an observable velocity of crystallization to occur. Because of this, such substances can crystallize by themselves from a solution or fused mass. Experience shows that the tendency to spontaneous crystallization decreases fairly rapidly with increasing length of chain. In the case of really highly polymerized substances, the chains are considerably longer. The number of independent elements in the statistical problem is greater (100 to 300) and the probability curve correspondingly steeper. In such cases the natural variation phenomena no longer suffice to produce a correspondingly frequent occurrence of stretched or nearly fully stretched chains. Therefore the velocity of crystallization is very small, and no arrangement of the thread-molecules occurs of itself. The formation of almost fully stretched single chains (unlikely in itself) is promoted only by the application of some external stress. Then they may be brought into an oriented condition and so result in the formation of crystallites or micelles. Von Susich and later Thiessen and his collaborators have carried out a number of very fruitful measurements on the melting points of crystalline rubber at different degrees of stretching. These figures show clearly that at a given temperature the formation of oriented regions increases with increased stretching. The external stress in this case assists the variation phenomena in the formation of the inherently improbable chain form, which alone is suitable for crystallization.

VALUES OF THE PHYSICAL CONSTANTS OF RUBBER *

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I. INTRODUCTION

This paper presents a survey of published values of some of the basic physical constants of rubber. The survey was undertaken for the purpose of selecting for each constant the value which seemed to be the most reliable, and tabulating these values in a form convenient for use. In the course of the work it soon became evident that the survey would perform an equally important function by pointing out the many gaps in the present knowledge of rubber, and thereby would serve as a guide for the planning of future investigations. There are some constants of rubber for which no reliable determinations are available, and others which are not known with sufficient accuracy to meet the needs of industrial and scientific work. Even in cases where the constants have been measured with evident care, many of the values represent the result of a single investigation, and hence should be subjected to independent confirmation.

A survey by Whitby of the physical constants and other properties of rubber appeared in the "International Critical Tables" in 1927, and more recently Dawson and Porritt have published a monumental work, "Rubber, Physical and Chemical Properties," which includes virtually all measurements on rubber reported before 1934. The present paper differs in point of view from the comprehensive treatment of Dawson and Porritt, since the aim here is to select a single value for each physical constant. The scope of the present paper is relatively restricted, since it deals only with 16 properties which are of fundamental significance, and hence have values which may be regarded as constants of rubber rather than simply as characteristics of the particular sample under consideration. The aim is to present values selected particularly for their scientific interest rather than for their technical importance. For the sake of comparison with the selected values, an attempt has been made to include all published values of the 16 properties.

(1) Selection of Properties

In this work only those physical properties which can be specified by numerical values will be considered, and even of these a large number of the commonly measured properties of rubber will be excluded from the present discussion. One class of such properties consists of those which cannot be exactly defined, or which can be defined only in terms of one particular type of equipment by which they are measured. This class is illustrated by such qualities as hardness, brittleness, plasticity, resistance to abrasion, resistance to tear, fatigue and the like.

A second class of properties not considered in this work includes those for which the values obtained show such variation that they must be regarded as characteristic of the specimen itself; that is, the values may depend, for example, on the size, purity or previous history of the specimen, and cannot be regarded as characteristic of rubber in general. In this class one finds almost all the tensile

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properties, aging properties and electrical breakdown properties which are commonly measured. These properties owe their extensive use in practical testing to the fact that they depend to such a large extent on the particular sample.

The distinction between the excluded properties and those which are treated here is not absolute, and in the future it may be possible to make additional inclusions or even certain omissions.

(2) Selection of Values

Since in many cases very few different observers have reported values taken under comparable conditions, no attempt has been made to utilize average values. The single value that seems to be the most reliable has been selected, but it should not be regarded as being final in any sense or, except as shown in specific cases, as having been verified by independent observers. Consequently, at present the selection must be somewhat arbitrary and must be based on internal evidence in the original published work, such as the method employed, the number of specimens investigated, the ranges of variables covered and similar factors. In most cases it is not possible within the limits of the present work to discuss these bases of selection, desirable as such a discussion might be.

In view of the limited number of measurements on which these values are based, it has not been found possible to give values of the probable errors of the constants. In each case the last figure is doubtful, and in many cases the last two figures are uncertain.

Values of the constants are given for a pressure of one atmosphere and a temperature of 25° C., corrections having been made where the direct observations were reported for other conditions. This temperature is widely used because of the convenience of maintaining it by thermostatic control. Wherever possible, the rate of change of the property with respect to temperature at 25° C. is also given.

(3) Forms of Rubber Considered

Consideration will be given here to rubber in four forms: purified hydrocarbon, commercial raw rubber, soft vulcanized rubber containing 2% combined sulfur and hard rubber containing 32% combined sulfur.

Commercial raw rubber in either of its usual forms, smoked sheet or pale crepe, consists of about 93% rubber hydrocarbon and about 7% other components. Some of the physical properties of raw rubber are influenced considerably by the presence of the nonhydrocarbon components, while others are influenced relatively little. Many of the values utilized here represent determinations made at the United States National Bureau of Standards on rubber which had been purified by digesting it with water at about 190° C. and subsequently extracting the protein-hydrolysis products, resins, salts and certain other components by water and alcohol[1]. The nonhydrocarbon content was thereby reduced to less than 0.5%. Values observed for the unpurified raw rubber are given also, when they are available.

In the case of certain constants of vulcanized rubber, observations have been reported over the complete range of sulfur content from 0 to 32%. For simplicity, only two compounds are treated here: the first a "pure-gum" soft-rubber compound containing 2% combined sulfur, the second an ebonite or hard rubber containing 32% sulfur. The first is not in itself a practical compound, but was selected because it is simple and, in regard to the physical properties considered here, is comparable to practical soft rubber compounds. In making these compounds, rubber was mixed with sulfur and vulcanized until substantially all the

TABLE I—PHYSICAL CONSTANTS OF RUBBER
(1 atmosphere, 25° C.)

Constant	Unit*	Multiply values by	Purified rubber	Ref.	Commercial raw	Ref.	Soft vulcanized 2% S	Ref.	Hard rubber 32% S	Ref.
Unit cell	Ångström unit		a = 8.54 ± 0.05 b = 8.20 ± 0.05 (fibre axis) c = 12.65 ± 0.05 β = 83°20′					2,3,4		
Density ρ (Table II)	g. cm.$^{-3}$		0.9060	1	0.911	5	0.923	6	1.173	6
$\frac{d\rho}{dT}$	g. cm.$^{-3}$.deg.$^{-1}$	× 10^{-6}	−595	1	−620	5	−611	6	−241	6
Expansivity $\frac{1}{V}\frac{dV}{dT}$ (Table III)	deg.$^{-1}$	× 10^{-6}	670	7	670[d]		661	6	194	8 6
$\frac{d}{dT}\left(\frac{1}{V}\frac{dV}{dT}\right)$	deg.$^{-2}$	× 10^{-9}	700	7	700[d]				500[a]	8
Thermal. Thermal Conductivity (Table IV)	 j. sec.$^{-1}$.cm.$^{-1}$.deg.$^{-1}$ cal. sec.$^{-1}$.cm.$^{-1}$.deg.$^{-1}$	 × 10^{-6} × 10^{-6}			 1340 320	 9,12 13	 1430[b] 342[b]	 10	 1625[a] 388[a]	 11
Specific heat, Cp	j. g.$^{-1}$.deg.$^{-1}$ cal. g.$^{-1}$.deg.$^{-1}$		1.880 0.449	14			2.14[c] 0.510[c]	15	1.43[c] 0.341[c]	15
$\frac{dCp}{dT}$	j. g.$^{-1}$.deg.$^{-2}$ cal. g.$^{-1}$.deg.$^{-2}$	× 10^{-3} × 10^{-3}	5.0 1.2	14						
Heat of fusion at 11° C.	j. g.$^{-1}$ cal. g.$^{-1}$		16.7 3.99	14						
Heat of combustion (Table V)	j. g.$^{-1}$ cal. g.$^{-1}$	× 10^3 × 10^3	45.25 10.82	16			44.45 10.63	16	33.11 7.92	16

Mechanical.										
Compressibility, $\frac{1}{V}\frac{dV}{dP}$	bar^{-1}	$\times 10^{-6}$	53.7	6			51.0	6	24.3	6
$\frac{d}{dT}\left(\frac{1}{V}\frac{dV}{dP}\right)$	bar^{-1}.deg.$^{-1}$	$\times 10^{-9}$	260	6			262	6	110	6
Poisson's ratio (elongation $<300\%$)							0.500[b]	17	0.2	18
Velocity of sound, v	m. sec.$^{-1}$						37[a]	19	1560[a]	20
$\frac{dv}{dT}$	m. sec.$^{-1}$.deg.$^{-1}$						-0.244[a]	19		
Optical.										
Refractive index, n_D (Table VI)			1.5190	21	1.5190[d]		1.5264	21	1.6[a]	22, 8
$\frac{dn_D}{dT}$	deg.$^{-1}$	$\times 10^{-6}$	350	21	350[d]		350	21		
Dispersion, $n_{4861} - n_{6563}$			0.0330	21						
Stress-optical coefficient	brewster						2100[b]	23	106[a]	24
Electrical.										
Dielectric constant (at 1,000 cycles per second)			2.37	25, 1	2.45	5	2.68	25	2.82	25
Power factor (at 1,000 cycles per second)		$\times 10^{-3}$	1.6	25	1.8	25	1.8	25	5.1	25
Conductivity (1-minute)	mho. cm.$^{-1}$	$\times 10^{-18}$	23	25	420	25	13	25	15	25

[a] Composition unspecified.
[b] Compound contained accelerators, etc.
[c] Mean value, between 25° and 175° C.
[d] Value for purified rubber used here, since purification has been shown to have negligible effect on the value.

*Abbreviations:—

cal.	calorie (4.1833 joules).	j.	joule.
cm.	centimeter.	m.	meter.
deg.	degree centigrade.	sec.	second.
g.	gram.		

sulfur had become combined, the process requiring at least 15 hours. In a few cases, specifically mentioned, accelerators were used, with a corresponding shortening of the time of vulcanization.

II. GENERAL TABLE OF CONSTANTS

The complete set of values selected for the physical constants is given in Table I. The remainder of this paper is devoted to a discussion of the individual values and a comparison of the selected values with other observations.

III. DIMENSIONS OF UNIT CELL

Unvulcanized rubber, if kept at a temperature between 10° C. and −40° C. for a sufficient length of time, is subject to a crystallization which causes a change in its properties. Vulcanized rubber has not been observed to crystallize in this manner but crystallization is produced by stretching either unvulcanized or soft vulcanized rubber beyond a certain limit. In all these cases no significant differences in the sizes of the unit cells have been found by x-ray measurements.

The observations and analysis of Lotmar and Meyer[2] may be regarded as superseding previous work in this field. They conclude that the unit cell, containing eight C_5H_8-units, is monoclinic and has the dimensions given in Table I. The *b* or fibre axis is the direction of stretch, and β is the angle between the *c* and *a* axes. These results, obtained apparently from stretched rubber of unspecified composition, were confirmed by Barnes[3] for frozen raw rubber melting at 41° C., and by Clark, Wolthuis and Smith[4] for stretched rubber and rubber crystallized from solution in ether, as well as that crystallized without a solvent. With one possible exception, the agreement with the analysis and measurements of Lotmar and Meyer was entirely within the range of experimental error.

IV. DENSITY AND EXPANSIVITY

(1) Density

The results of measurements of density and specific gravity are summarized in Table II. The results for specific gravity have been referred to water at 4° C. in order to give a quantity numerically equal to the density in g. per cc. Where necessary, the densities were corrected to 25° C. by use of the temperature coefficient given in Table I.

In the case of the purified rubber, it should be pointed out that the method of purification employed by Weber[26] and by Macallum and Whitby[27] differed from the method used by McPherson[1] and by Scott[6]. No details were given regarding the method of purification used by Bondy[28]. To obtain a value of the density of purified rubber from Scott's data, extrapolation of the combined sulfur content from 3% to zero was necessary.

The variations shown in the density of raw rubber probably represent real differences in the samples and not accidental errors of observation. With only two exceptions the values lie between 0.905 and 0.919 g. per $cm.^{-3}$.

The change in density on vulcanization is a matter of considerable practical interest. The following comparison of values from Table II indicates that the change on vulcanization with 2% sulfur is the same in the case of purified rubber as for crude or commercial raw rubber:

	Density $g.\text{-}cm.^{-3}$		
Kind of rubber	Unvulcanized	Vulcanized	Difference
Crude	0.911	0.928	0.017
Purified	0.9060	0.923	0.017

TABLE II

DENSITY

Observer	Date	Ref.	Numerical value reported [e]	Temp.	Density at 25° C. g.-cm.$^{-3}$
Purified rubber.					
Weber	1903	26	0.911	17° C.	0.905
Macallum and Whitby	1924	27	0.9237	20° C.	0.9207
Bondy (Staudinger)	1930	28	0.9238	20° C.	0.9208
McPherson	1932	1	0.9060	25° C.	0.9060*
Scott	1935	6	0.9078[f]	25° C.	0.9078
Mean value for purified rubber					0.9121
Unpurified raw rubber.					
Weber	1903	26	0.915[c]	17° C.	0.909
			0.931[d]	17° C.	0.925
Bunschoten	1921	29	0.912	15° C.	0.905
			0.915	15° C.	0.908
			0.917	15° C.	0.910
Kirchhof and Matulke	1924	30	0.920	20° C.	0.917
Macallum and Whitby	1924	27	0.9217	20° C.	0.9186
Van Rossem	1924	31	0.909	25° C.	0.906
Geiger	1925	32	0.920	16° C.	0.914
Feuchter	1926	33	0.935	15° C.	0.928
Curtis, McPherson and Scott	1927	5	0.9112	25° C.	0.911*
Feuchter and Hauser	1929	34	0.917	15° C.?	0.910
Van Rossem and Lotichius	1929	35	0.920	15° C.	0.913
Kimura and Namikawa	1929	36	0.908	25° C.	0.908
Bekkedahl and Wood[g]	1937	—	0.914	25° C.	0.914
Whitby	1937	37	0.913	15° C.	0.906
			0.917	15° C.	0.910
			0.922	15° C.	0.915
			0.925	15° C.	0.918
Whitby	1937	38	0.923	15° C.	0.916
			0.918	15° C.	0.911
Mean value for unpurified raw rubber					0.9130
Soft vulcanized compound, 2% sulfur.					
Curtis, McPherson and Scott	1927	5	0.928[a]	25° C.	0.928
Kimura and Namikawa	1929	36	0.925[a]	25° C.	0.925
Scott	1935	6	0.923[b]	25° C.	0.923*
Mean value for soft vulcanized rubber					0.925
Hard rubber, 32% sulfur.					
Curtis, McPherson and Scott	1927	5	1.172[a]	25° C.	1.172
Kimura and Namikawa	1929	36	1.174[a]	25° C.	1.174
Church and Daynes	1935	39	1.177[a]	15° C.	1.175
Scott	1935	6	1.173[b]	25° C.	1.173*
Mean value for hard rubber.					1.174

* Value selected for Table I.
[a] Compound of unpurified raw rubber and sulfur.
[b] Compound of purified rubber and sulfur.
[c] Lowest value.
[d] Highest value.
[e] Specific gravity in most cases.
[f] Value extrapolated from vulcanized compounds to 0% sulfur.
[g] Unpublished work.

The determinations for crude rubber were both reported in the same paper, whereas those for purified rubber were given by different investigators in the same laboratory.

From the values reported, the density of hard rubber does not seem to be significantly altered by the purification of the rubber used in its preparation.

For the rate of change of density with temperature at 25° C., use has been made of the values given by the data of the respective observers whose density values have been selected for Table I. In the case of the vulcanized rubber, the data relate to the observed rate of change of specific volume with temperature. It may be readily shown that, at temperature T:

$$\frac{d\rho}{dT} = -\frac{1}{V_a^2}\frac{dV_a}{dT} \tag{1}$$

Here ρ and V_a are, respectively, the density and its reciprocal, the specific volume, of the material under consideration. The insertion of Scott's data[6] in equation 1 yields the values given in Table I for the soft vulcanized rubber and for hard rubber.

(2) Expansivity

The volume thermal expansivity of a material is defined as $\frac{1}{V}\cdot\frac{dV}{dT}$, where T is the temperature and V the volume of the material under consideration. The term coefficient of volume expansion is often defined to be the same as the expansivity, although sometimes it is limited to the value of the expansivity at 0° C., and sometimes it is used to mean merely dV_a/dT, where V_a is the specific volume.

Values of the expansivity of rubber, as computed from observations in the literature, are given in Table III. Where, in the original work, the values were reported in terms of rate of change of density with temperature, the expansivity was computed from the relation:

$$\frac{1}{V}\frac{dV}{dT} = -\frac{1}{\rho}\cdot\frac{d\rho}{dT} \tag{2}$$

Since there seems to be no significant change of expansivity on purification of the raw rubber, the values have not been classified under separate headings.

The values obtained in investigations of soft rubber compounds containing up to 5% sulfur have been grouped with those for compounds of 2% sulfur content, since the work of Scott[6] indicates a negligible variation of expansivity with sulfur content in this range. None of the observers working with soft vulcanized rubber obtained data from which the temperature coefficient may be obtained. Therefore in this case the values could not be corrected to correspond to a temperature of 25° C.

In the three cases in which the linear expansion of hard rubber was measured, since there was no indication that the material had different properties in different directions, the reported values of linear expansivity have been multiplied by three to obtain the volume expansivity—a familiar procedure, readily justified in the present instance.

It is difficult to determine the rate of variation of expansivity with temperature, since it involves the second derivative of directly observed quantities. For hard rubber, the value obtained from the observations of Dorsey[45] is about 430×10^{-9} deg.$^{-2}$, which may be compared with the value in Table I.

TABLE III

VOLUME EXPANSIVITY

Observer	Date	Ref.	Temp. range investigated	Value reported deg.$^{-1}$ $\times 10^{-6}$	Corresponding mean temp.	Expansivity at 25° C. deg.$^{-1}$ $\times 10^{-6}$
Raw rubber.						
Russner	1882	40	20–30° C.	668[b]	25° C.	668
Curtis, McPherson, and Scott	1927	5	15–40° C.	680[c, k]	27.5° C.	678
Kimura and Namikawa	1929	36	0–85° C.	620[c]	30° C.	617
McPherson	1932	1	0–60° C.	657[d]	30° C.	654
Bekkedahl	1934	7	− 72 to + 85° C.	670[d]	25° C.	670*
Scott	1935	6	10–85° C.	662[d, k]	47.5° C.	651
Mean value for raw rubber	—	—	—	—	—	656
Soft vulcanized rubber.						
Lebedev	1881	41	—	670[a]	—	—
Lundal	1898	42	0–60.7° C.	763[f]	30° C.	—
	—	—	—	562[f]	30° C.	—
Curtis, McPherson, and Scott	1927	5	15–40° C.	670[e]	27.5° C.	—
Kimura and Namikawa	1929	36	0–85° C.	615[e]	42.5° C.	—
Bekkedahl	1934	7	− 70 to + 40° C.	650[d, e]	—15° C.	—
Dawson and Parris	1935	43	12–30° C.	654[g]	21° C.	—
Scott	1935	6	10–85° C.	661[d, e]*	47.5° C.	—
Holt and McPherson	1936	17	− 20 to + 100° C.	656[e, i, m]	25° C.	—
Hard rubber, 32% sulfur.						
Kohlrausch	1873	44	17–25° C.	231[a, j]	21° C.	233
	—	—	25–35° C.	253[a, j]	30° C.	251
Mayer	1891	8	0–100° C.	194[h]	25° C.	194*
Dorsey	1908	45	− 180 to + 20° C.	202[a, j]	0° C.	214
Souder and Hidnert	1919	46	20–60° C.	240[a, j]	40° C.	232
Curtis, McPherson and Scott	1927	5	15–40° C.	200	27.5° C.	199
Kimura and Namikawa	1929	36	0–85° C.	150	20° C.	153
	—	—	—	170	40° C.	163
	—	—	—	200	60° C.	183
	—	—	—	270	80° C.	247
Church and Daynes	1935	39	20–50° C.	197	35° C.	192
Scott	1935	6	10–85° C.	205[d]	47.5° C.	194*
Mean value for hard rubber	—	—	—	—	—	205

* Value selected for Table I.
[a] Composition unspecified.
[b] Para rubber.
[c] Smoked sheet.
[d] Purified rubber.
[e] Compound contained 2% sulfur.
[f] "Grey rubber, containing 2.5-3% sulfur."
[g] Compound contained 5.26% sulfur.
[h] Compoud contained 34% sulfur.
[i] Compound contained accelerators, etc. (compound described in section on Poisson's ratio).
[j] Linear expansion measured.
[k] Value extrapolated from vulcanized compounds to 0% sulfur.
[m] Calculated value for 25° C.

V. THERMAL CONSTANTS

The thermal constants here considered have been expressed in Table I in terms of both joule and calorie, since both appear in the literature. Modern precise measurements in this field are made with electrical energy, and the immediate results are obtained in joules. For conversion, one calorie has been taken equal to 4.1833 international joules, a value representing very nearly the 15-degree calorie which has been extensively used[47].

(1) Thermal Conductivity

Thermal conductivity is defined as the amount of heat per unit time passing by conduction across unit area and through unit thickness of a material, for unit temperature difference in the direction of the thickness. This constant is of considerable technical importance in the case of rubber, but unfortunately there seem to be experimental difficulties in obtaining data of high accuracy. The elimination of thermal resistance at the contacts, for example, by the exclusion of air films at the surfaces, is a point of particular importance.

A summary of the results of measurements on rubber is given in Table IV. Only in the case of hard rubber can a temperature coefficient be evaluated. Van Dusen[11], chiefly on the basis of the data by Eucken[48], gives a figure of about 960×10^{-9} j.sec.$^{-1}$.cm.$^{-1}$.deg.$^{-2}$ (224×10^{-9} cal.sec.$^{-1}$.cm.$^{-1}$.deg.$^{-2}$).

(2) Specific Heat

The heat capacity, or specific heat at constant pressure, has been measured by several observers, but the work of Bekkedahl and Matheson[14] on purified hydrocarbon seems for our purpose to supersede all previous work on the subject. Their measurements are particularly notable, compared with those previously reported, with respect to recognition of the existence of a crystalline form of the hydrocarbon, in the range of temperature covered, in the reproducibility of the results and in the accuracy made possible by the apparatus employed.

The observations of McPherson and Bekkedahl[15] yield equations from which the mean specific heat of vulcanized rubber between 25° and 175° C. corresponding to any desired percentage of sulfur may be calculated. It should be particularly noted that the values, which are given in Table I, do not correspond to a temperature of 25° C., but are the mean specific heat over the range from 25° to 175° C. Joule[61] has given a value of 0.415 cal. g.$^{-1}$.deg.$^{-1}$ (1.735 j.g.$^{-1}$.deg.$^{-1}$) for soft vulcanized rubber. Mayer[8] made measurements on hard rubber by the method of mixtures, obtaining a reported value of 0.33125 cal.g.$^{-1}$.deg.$^{-1}$ for a mean temperature somewhat below 100° C. Stephens[60] found 0.33 cal.g.$^{-1}$.deg.$^{-1}$ at 12° C.

The work of Bekkedahl and Matheson[14] showed that, in the neighborhood of 25° C., the specific heat is approximately a linear function of the temperature with the rate of change given in Table I.

(3) Heat of Fusion of Crystalline Rubber at 11° C.

Fusion of crystalline rubber hydrocarbon at a temperature of the order of 11° C. was found by Bekkedahl and Matheson[14] to be characterized by an absorption of heat of 16.71 j.g.$^{-1}$ (3.99 cal. g.$^{-1}$). This may be compared with the value 21.1 j.g.$^{-1}$ (5.05 cal.g.$^{-1}$) for the difference between the heats of swelling of frozen and thawed raw rubber, observed by van Rossem and Lotichius[35]. On the assumption that rubber hydrocarbon can ordinarily be only partly crystallized, Parks[62] has made a calculation from the data of Bekkedahl and Matheson to obtain a heat of fusion of about 72.8 j.g.$^{-1}$ for the completely crystallized hydrocarbon.

TABLE IV

THERMAL CONDUCTIVITY

Observer	Date	Ref.	Mean temp. or range	Reported value, cal.sec.$^{-1}$. cm.$^{-1}$.deg.$^{-1}$ $\times 10^{-6}$	Conductivity at 25° C. cal.sec.$^{-1}$. cm.$^{-1}$.deg.$^{-1}$ $\times 10^{-6}$
Raw rubber.					
Lees	1892	49	25–30° C.	380	—
Griffiths and Kaye	1923	9	25° C.	320*	
Williams	1923	12	45–100° C.	320*	—
Barnett	1934	13	—	320*	—
Mean value for raw rubber.	—	—	—	335	—
Soft vulcanized rubber.					
Herschel, Lebour, and Dunn	1879	50	49° C.	340[b]	—
—	—	—	46° C.	440[c]	—
Van Dusen	1920	51	—	420[e]	—
A.S.T.M.	1930	10	—	343[d]*	—
Weh	1937	52	45° C.	361[e]	—
Mean value for soft vulcanized rubber	—	—	—	381	—
Hard rubber.					
Herschel, Lebour, and Dunn	1879	50	49° C.	360[e]	355
—	—	—	—	380[e]	375
Lees	1892	49	25–35° C.	400[e]	399
Lees	1898	53	33° C.	424[e]	422
—	—	—	51° C.	410[e]	404
—	—	—	63° C.	398[e]	389
Dina	1899	54	6–90° C.	375[e]	370
Eucken	1911	48	–190° C.	330[e]	378
—	—	—	–78° C.	365[e]	388
—	—	—	0° C.	371[e]	377
Niven and Geddes	1912	55	20° C.	421[e]	422
Barratt	1915	56	20° C.	136[e]	137[a]
—	—	—	100° C.	131[e]	114[a]
Giacomini	1918	57	0° C.	378[e]	384
Taylor	1919	58	25–50° C.	380[e]	377
Van Dusen	1929	11	25° C.	388[e]	388*
Vernotte	1932	59	—	410[e]	410
Stephens	1933	60	17° C.	415[e]	417
Mean value for hard rubber.	—	—	—	—	394

* Value selected for Table I.
[a] Value omitted in computing mean.
[b] Sample of "red rubber."
[c] Sample of "grey rubber, nearly pure caoutchouc."
[d] Sample approximately the same as the compound described in the section on Poisson's ratio.
[e] Composition unspecified.

(4) HEAT OF COMBUSTION

The heat of combustion of rubber has been determined by a number of investigators, whose results are summarized in Table V. In all cases, unless indicated otherwise, the rubber was purified in some manner. All values have been made to refer to combustion at a constant pressure of one atmosphere, and at a temperature of 25° C. when the temperature was given.

Jessup and Cummings[16] observed a considerable variation in results from samples having different nonhydrocarbon contents. In general the heat of combustion, corrected for ash content, was found to be reduced by the presence of impurities. The value utilized here for unvulcanized rubber is based on that given by Jessup and Cummings for the average of a number of measurements on two samples of rubber purified by the method of McPherson[1] and having ash contents

of 0.02 and 0.03%. The value is very nearly the same as that obtained, by extrapolation to zero ash content, from the results of measurements on thirteen samples purified by several different methods.

The heats of combustion of rubber-sulfur compounds were calculated by means of the linear equation which was found to represent the results of Jessup and Cummings.

For the calculation of the temperature coefficient of the heat of combustion in this region, values of specific heats were taken from Bekkedahl and Matheson[14] for rubber, and from "International Critical Tables"[68, 69] for the other reactants. The result obtained for unvulcanized rubber is -2.24 j.g.$^{-1}$.deg.$^{-1}$; that is, the heat of combustion decreases by 2.24 j.g.$^{-1}$ for each degree rise of temperature. Similarly the temperature coefficient of the heat of combustion of the soft vulcanized rubber has been calculated to be -2.21 j.g.$^{-1}$.deg.$^{-1}$ and that for the hard rubber -1.77 j.g.$^{-1}$.deg.$^{-1}$.

Table V

Heat of Combustion

Observer	Date	Ref.	Value reported, constant volume, cal.g.$^{-1}$. $\times 10^3$	Heat of combustion at constant pressure, j.g.$^{-1}$ $\times 10^3$
Raw rubber				
Weber	1903	63	10.669	44.71
Kirchhof and Matulke	1924	30	10.70	44.84
Schläpfer (Geiger)	1925	64	10.70[c]	44.84
Messenger	1929	65	10.97	45.97
Blake	1930	47	10.547[b]	44.20
Hada, Fukaya, and Nakajima	1931	66	10.495	43.98
Endoh	1932	67	10.703	44.85
Jessup and Cummings	1934	16	(45.239)[a]	45.25*
Mean value for raw rubber	—	—	—	44.83
Soft vulcanized compound, 2% sulfur.				
Blake	1930	47	10.395[b]	43.56
Hada, Fukaya, and Nakajima	1931	66	10.45	43.79
Jessup and Cummings	1934	16	(44.44)[a]	44.45*
Mean value for soft vulcanized rubber	—	—	—	43.93
Hard rubber, 32% sulfur.				
Blake	1930	47	8.268[b]	34.66
Jessup and Cummings	1934	16	(33.10)[a]	33.11*
Mean value for hard rubber	—	—	—	33.88

* Value selected for Table I.
[a] In joules per g., at constant pressure.
[b] Rubber not purified.
[c] It is not clear whether this value represents an independent determination or is the same as the determination of Kirchhof and Matulke[30].

VI. MECHANICAL CONSTANTS

(1) Volume Compressibility

The compressibility is defined as $\frac{1}{V}\frac{dV}{dP}$, where V is the volume of material under consideration at a pressure P. The pressure is a force per unit area acting in all directions, and the compressibility bears no direct relation to the socalled "compression" tests of rubber, in which the material is free to move in a direction transverse to the force.

Early measurements of the compressibility of rubber relative to that of other substances yielded contradictory results. Adams and Gibson[70] in recent work at pressures about 1000 bars (the bar is defined as 10^6 dynes.cm.$^{-2}$, and is thus equal to 0.987 normal atmosphere), measured the compressibilities of compounds containing fillers and of a single rubber-sulfur compound containing 10% sulfur. Scott[6] has made measurements on the complete system of rubber-sulfur compounds at pressures below 1000 bars. The equations representing the observations of Scott have therefore been used here to obtain the compressibilities under the standard conditions of this work.

The temperature and pressure coefficients of compressibility have also been calculated from the same equations. The difference between the values of compressibility at one atmosphere and those at a pressure of zero can thus be seen to be considerably less than the experimental error of the determination.

(2) Poisson's Ratio

Of the large number of investigators who have studied the change of volume of vulcanized rubber on stretching, very few have worked with specimens which were free from coarse fillers and other inhomogeneities of such character as to cause the formation of vacuoles on stretching and thus mask any changes in the rubber itself. The samples studied by many of the recent observers contained fillers, and, in much of the early work, the "pure-gum" compounds studied doubtless contained particles of uncombined sulfur.

A "pure-gum" compound investigated by Holt and McPherson[17] seems to have been relatively free from inhomogeneities. It had the following composition:

	Parts by weight
Rubber	100
Sulfur	2
Zinc oxide	1
Stearic acid	1
Tetramethylthiuram disulfide	0.3

Vulcanization: 30 minutes at 126° C.

For this compound, and for others free from coarse particles, there was found to be no change in volume on stretching to an elongation of about 300%. Above this point there was a decrease of volume, corresponding to fibre formation or crystallization, which has already been mentioned in connection with the unit cell.

Poisson's ratio is defined as the ratio of an infinitesimal fractional decrease in a transverse dimension to the corresponding infinitesimal fractional increase in the longitudinal dimension of a specimen on the application of a force in the direction of the longitudinal dimension. These observations on change of volume show that for elongations of 300% or less, Poisson's ratio for rubber lacking inhomogeneities is 0.500. For elongations above 300%, Poisson's ratio was found to be greater, a value as large as 0.527 being observed. For hard rubber of unspecified composition, a value of 0.2, calculated from measurements on the modulus of rigidity, is reported by Adams and Heaps[18].

(3) Velocity of Sound

The velocity of a compressional wave in general, or of a sound wave in particular, is a constant of interest not only in itself, but also as yielding information

about rubber under conditions which are as nearly as possible adiabatic and without plastic flow.

The work done by Exner[19] in 1874 seems to have been performed with considerable care, and to be of some significance in spite of the very limited equipment available at that period. From observations at a number of different temperatures, interpolation yielded at 25° C. a value of 37 m.sec.$^{-1}$ for a compound of unknown composition. The specimen was described merely as a rod of gray vulcanized rubber. In this region the velocity was found to decrease with increase of temperature at a rate of 0.244 m.sec.$^{-1}$.deg.$^{-1}$.

For hard rubber with a density of 1.25 g.cm.$^{-3}$, Irons[20] reports a value of 1560 m.sec.$^{-1}$ at a temperature of 18° C., in agreement with 1573 m.sec.$^{-1}$ at 14° C., a value obtained[71] from data of Campanile[72].

VII. OPTICAL CONSTANTS

(1) Refractive Index

The refractive index of unvulcanized rubber, determined by different observers, is given in Table VI. From this table, it can be seen that the index depends but little on the origin, preparation or purification of the rubber.

For vulcanized rubber containing 2% sulfur, an equation given by McPherson and Cummings[21] to represent their experimental data yields a value of 1.5624. This relation was first given in a preliminary report in the "Technical News Bulletin" of the National Bureau of Standards[73]. This report was translated by Kirchhof for *Kautschuk*[74], and his article in turn was translated back into English for *Rubber Chemistry and Technology*[74]. Some authors have mistakenly attributed the values in Kirchhof's article[74] to Kirchhof himself, since they differ slightly from the final values reported by McPherson and Cummings[21].

Reliable values for the refractive index of hard rubber seem to be lacking, probably because of its low transmission in the visible range. Mayer[8] has reported a value of 1.568 for light of unspecified composition from measurements of the polarizing angle. Ayrton and Perry[22] report a value of 1.611 from similar measurements made by Jellett. By refraction of red light with a 28.5° hard rubber prism, Ayrton and Perry found a refractive index of 1.66.

Kirchhof[75] investigated the refractive index of a number of widely different types of raw rubber at different temperatures. The values of the rate of change of refractive index with temperature at 25° C. ranged from 300×10^{-6} to 420×10^{-6} deg.$^{-1}$ with 369×10^{-6} deg.$^{-1}$ as the mean of 8 values. McPherson[1] gives 360×10^{-6} deg.$^{-1}$ in preliminary work on purified rubber, and the more extended work of McPherson and Cummings[21] indicates a value of 350×10^{-6} deg.$^{-1}$ as valid not only for purified rubber, but also for compounds of rubber and sulfur containing up to 16% of sulfur.

(2) Dispersion

The refractive indices mentioned up to this point, with the exception of those for hard rubber, have all been measured with light of a wave length of approximately 5893 Ångström units (sodium D-lines). The dispersion, defined as the difference between the refractive indices measured at two arbitrary wave lengths, seems to have been measured only by McPherson and Cummings[21]. They employed the commonly used wave lengths of 6563 Ångström units (hydrogen α or Fraunhofer C line) and 4861 Ångström units (hydrogen β or Fraunhofer F line), and reported a value of 0.0330. The value of the refractive index at the longer wave length is probably influenced by the proximity of an absorption band in the infrared.

TABLE VI

REFRACTIVE INDEX OF UNVULCANIZED RUBBER

Observer	Date	Ref.	Reported value n_D^T	Temp. T	Index at 25° C. n_D^{25}
Evaporated latex.					
Kirchhof	1932	75	1.5190	25° C.	1.5190
McPherson and Cummings	1935	21	1.5190	25° C.	1.5190
Mean value	—	—	—	—	1.5190
Para rubber.					
Curtis and McPherson	1925	76	1.520	25° C.	1.520
Kirchhof	1932	75	1.5220	20° C.	1.5202
Mean value	—	—	—	—	1.5201
Pale crepe.					
Twiss	1923	77	1.525	15° C.	1.521
Curtis and McPherson	1925	76	1.519	25° C.	1.519
Shacklock	1932	78	1.5248	20.8° C.	1.5233
Kirchhof	1932	75	1.5200	25° C.	1.5200
McPherson and Cummings	1935	21	1.5187	25° C.	1.5187
Mean value	—	—	—	—	1.5205
Smoked sheet.					
Macallum and Whitby	1924	27	1.5208	20° C.	1.5190
Curtis and McPherson	1925	76	1.519	25° C.	1.519
Tanaka	1927	79	1.5205	20° C.	1.5187
Kirchhof	1932	75	1.5182	25° C.	1.5182
McPherson and Cummings	1935	21	1.5188	25° C.	1.5188
Mean value	—	—	—	—	1.5188
Purified rubber.					
Macallum and Whitby	1924	27	1.5219[c]	20° C.	1.5201
Geiger	1925	32	1.5222	16° C.	1.5191
Kirchhof	1932	75	1.5222[d]	20° C.	1.5204
	—	—	1.5225[e]	20° C.	1.5207
	—	—	1.5220[b]	20° C.	1.5202
McPherson	1932	1	1.5184[a]	25° C.	1.5184
Smith, Saylor, and Wing	1933	80	1.525[d]	11° C.	1.520
McPherson and Cummings	1935	21	1.5190[a]	25° C.	1.5190*
Mean value	—	—	—	—	1.5197

* Value selected for Table I.
[a] Purified by method of McPherson.[1]
[b] Purified by method of Pummerer.
[c] Purified by acetone extraction and precipitation from benzene.
[d] Sol rubber.
[e] Gel rubber.

(3) STRESS-OPTICAL COEFFICIENT

In common with a number of other materials, rubber under stress exhibits the property of double refraction. Light passing at normal incidence through a sheet of rubber under stress is split up into two plane-polarized rays called ordinary and extraordinary rays. The velocities of these rays, as evidenced by the indices of refraction, differ, so that there is a phase difference between the rays as they emerge. The amount of phase difference, or retardation of one ray with respect to the other, is proportional to the thickness of the rubber and to the stress, provided the stress is uniform over any section normal to the sheet, shearing stresses being absent. The proportionality constant is known as the stress-optical coefficient of the material. (For the more general case of non-uniform stresses the

retardation is proportional to the thickness and to the difference of principal stresses, with the same factor of proportionality, namely, the stress-optical coefficient[81].) In other words, the stress-optical coefficient is equal to the relative retardation per unit thickness produced by unit stress under these conditions. When the relative retardation is expressed in Ångström units, the stress in bars (1 bar$=10^6$/dynes.cm.$^{-2}=1.0197$ kg.cm.$^{-2}$), and the thickness in millimeters, the stress-optical coefficient is given in terms of a unit called the brewster. A brewster is 10^{-13} cm.^{2}.dyne^{-1}.

The stress-optical coefficient of the soft vulcanized rubber compound already described in the section on Poisson's ratio has been measured by Thibodeau and McPherson[23]. The mean value obtained from seven specimens was 2096 brewsters. In other work[81] on a single specimen over a much smaller range of stresses, a value of 2030 brewsters was reported. For hard rubber a value of 106 brewsters has been reported without any further details[24].

VIII. ELECTRICAL CONSTANTS

(1) Dielectric Constant

The term dielectric constant is defined in terms of the repulsion between point charges of electricity, but is generally measured as the ratio of the capacitance of a capacitor (condenser) having the material as its dielectric to that of an air capacitor, otherwise identical. Dielectric constant is numerically equal to specific inductive capacity or permittivity. All values considered here were measured at a frequency of 1000 cycles per second.

The dielectric constant of purified rubber has been reported[25] as 2.37. This value represents the mean of 17 determinations, and is identical with that given by McPherson[1] for the mean of observations on 14 specimens differing in botanical origin and subsequent treatment. Some of the same observations are included in both averages.

The dielectric constant of commercial raw rubber is higher and shows a much greater variation from sample to sample. Values between 2.40 and 2.70 are obtained in most cases, the mean of eight determinations on smoked sheet being reported as 2.45[5]. The mean of 42 determinations on raw rubbers of differing preparation and treatment is given in an earlier paper by the same authors[76] as 2.46. The value read from graphs in another paper[82] from the same laboratory is also in agreement with these figures.

Compounds of rubber and sulfur, unlike pure rubber hydrocarbon, are thought to contain dipoles, originating in the carbon-sulfur linkage. Consequently the electrical characteristics of vulcanized rubber, compared with those of unvulcanized rubber, are much more complicated and correspond in general to those of polar compounds. With increasing sulfur content there is an increased number of dipoles, and at the same time a decreased freedom of rotation of the dipoles. These two factors usually produce opposite effects on electrical properties. Either factor may predominate depending on external conditions, such as temperature, pressure and electrical frequency employed. The property under consideration may have a maximum or minimum at some intermediate condition.

For the compound of purified rubber containing 2% sulfur, Scott, McPherson and Curtis[25] report for the dielectric constant a value of 2.68 as the average of two determinations. Earlier work by the same authors[5] on the same compound made from unpurified raw rubber gave a value of 2.67. In a paper[82] concerned with the effect of pressure on compounds of unpurified rubber, a value of 2.71 may be read from a graph. A somewhat higher value, about 2.8, can be obtained from the data

of Kitchin[83]. Boggs and Blake[84] in the same laboratory had previously given a graph from which a value of about 3.0 may be read.

Eight determinations of the dielectric constant of the compound of purified rubber containing 32% sulfur furnished a mean value of 2.82. The earlier work[5] involving five determinations on the unpurified rubber compound gave a value of 2.90, which is the same figure as is obtained from the graphs of Scott[82]. The previously mentioned graph of Boggs and Blake[84] shows a value of approximately 3.0.

The dielectric constant of unvulcanized rubber was found[25] to change with temperature at the rate of about -1×10^{-3} deg.$^{-1}$ at 25° C. The corresponding rate for a compound with 2% sulfur is of the order of -2.6×10^{-3} deg.$^{-1}$. For hard rubber containing 32% sulfur, the rate was found to be about $+0.6\times10^{-3}$ deg.$^{-1}$, the dielectric constant increasing with increase of temperature.

(2) Power Factor

When an alternating e.m.f. is applied to an ideal capacitor, having no power loss in the dielectric, the resulting current is 90° ahead of the e.m.f. In practical cases, particularly with solid dielectrics, there is a lower loss of magnitude EIF, where E and I are the e.m.f. and current respectively and F, thus defined, is the power factor. The power factor is the sine of the phase-difference angle ψ, the amount by which the phase angle differs from 90°. The power factor is observed to depend on the material, but not on the dimensions of the dielectric.

For purified unvulcanized rubber, the mean of 19 determinations[25] of the power factor was 1.6×10^{-3}. Since the effect of residual impurities, including moisture, is to increase the power factor, it is probable that the true power factor of rubber hydrocarbon itself is less than 0.8×10^{-3}, the lowest value observed in another series[1] of which the mean value was 1.5×10^{-3}. For unpurified rubber, the power factor is somewhat more variable. A mean of 34 observations in one case[76] and of eight observations in another[5] gave in each case a value of 1.8×10^{-3}.

With a compound of purified rubber containing 2% sulfur the mean of three determinations of power factor[25] was 1.8×10^{-3}. For a compound of unpurified raw rubber and sulfur, the corresponding figure, involving two determinations[5], was 3.1×10^{-3}.

The power factor of hard rubber made from purified rubber was found from 10 determinations[25] to have a value of 5.1×10^{-3}, while five determinations[5] on unpurified rubber compound gave a value of 8.8×10^{-3}.

The power factor of rubber may undergo large variations with change of temperature, with the occurrence of maxima and minima. However, for the unvulcanized rubber and for the two vulcanized compounds under consideration here, the rate of change of power factor with temperature at 25° C. is not large compared with its value under other conditions. It seems that no satisfactory estimate of its magnitude can be made from available data.

(3) Conductivity

The volume conductivity of a material is defined as the conductance through the material between opposite faces of a specimen of unit thickness and of unit cross-sectional area. Conductance, the reciprocal of resistance, is measured in reciprocal ohms or mhos. If the dimensions of the material are measured in centimeters, the unit of conductivity is the mho per centimeter.

The conductivity of rubber, like that of other insulating materials, varies greatly with the time which elapses between the application of the potential and

the measurement. The measurements discussed here were all made one minute after the application of the potential.

The conductivity of rubber varies greatly from one sample to another, and is much increased by impurities. It is possible that at normal temperatures the conductivity of rubber is due entirely to nonhydrocarbon components.

Sixteen determinations[25] of the conductivity of purified raw rubber yielded a mean of 23×10^{-18} mho.cm.$^{-1}$. Other work[1] on purified rubbers of different botanical sources gave 22×10^{-18} mho.cm.$^{-1}$ as the mean of 13 determinations, some of them the same as those just mentioned. The lowest value was 14×10^{-18} mho.cm.$^{-1}$. The mean of eight determinations on unpurified raw rubber[5] was about 570×10^{-18} mho.cm.$^{-1}$.

For the vulcanized compound of purified rubber, containing 2% sulfur, three determinations[25] gave a mean of 13×10^{-18} mho.cm.$^{-1}$ for the conductivity. Two samples of the corresponding compound from unpurified raw rubber were found[5] to possess a conductivity of about 300×10^{-18} mho.cm.$^{-1}$.

Hard rubber made from purified rubber and containing 32% sulfur was observed[25] from the mean of nine determinations to possess a conductivity of 15×10^{-18} mho.cm.$^{-1}$. When the rubber was not purified, five determinations[5] gave a mean of 47×10^{-18} mho.cm.$^{-1}$.

No significant value can be given for the temperature coefficient of conductivity at 25° C., because of the rapid change of the coefficient near this temperature.

IX. RELATIONS BETWEEN CONSTANTS

There are certain theoretical relations between some of the constants which have been considered. One of these relations, that between expansivity, density and rate of change of density with temperature, has already been mentioned, and is given by equation 2.

(1) Expansivity and Change of Refractive Index with Temperature

Another relation involves the rate of change of refractive index with temperature. The work of Eykman[85], supported by more recent results[86], has shown that for a single hydrocarbon at least, in the case of changes of refractive index n and density ρ caused by changes in temperature or pressure, the following equation, in which R is a constant, is valid very nearly within the limits of experimental error over the complete range of attainable values:

$$\frac{n^2-1}{n+0.4}=R\rho \tag{3}$$

By differentiation with respect to the temperature T and elimination of R, the following is derived:

$$\frac{dn}{dT}=-\frac{1}{\dfrac{2n}{n^2-1}-\dfrac{1}{n+0.4}}\left(\frac{1}{V}\frac{dV}{dT}\right) \tag{4}$$

The insertion of the values of expansivity and refractive index, taken from Table I, in the right-hand member of equation 4 gives in the case of purified rubber -367×10^{-6} deg.$^{-1}$, which may be compared with the value directly observed, *viz.*, -350×10^{-6} deg.$^{-1}$. The figures in the case of the 2% sulfur compound are -372×10^{-6} and -350×10^{-6} deg.$^{-1}$, respectively.

(2) Refractive Index and Dielectric Constant

The electromagnetic theory of light yields the following relation between the refractive index n and the dielectric constant ε of a medium of negligible magnetic susceptibility:

$$n^2=\varepsilon \tag{5}$$

where n and ε are measured at the same frequency. Since the frequency of light is of the order of 10^{14} sec.$^{-1}$ and the frequency here used in measuring ε is 10^3 sec.$^{-1}$, no strictly valid use can here be made of equation 5. However, in the case of purified rubber, the value of n^2 measured for the D-lines is 2.307, and that of the dielectric constant, as given in Table I, is 2.37. For the compound containing 2% sulfur the corresponding values are 2.330 and 2.68 respectively. For hard rubber the corresponding results are 2.6 and 2.82, respectively.

A differentiation of equation 5 with respect to temperature gives:

$$\frac{2n\,dn}{dT}=\frac{d\varepsilon}{dT} \tag{6}$$

For purified rubber the values in Table I yield -1.06×10^{-3} deg.$^{-1}$ as the left-hand member; this may be compared with -1×10^{-3} deg.$^{-1}$, directly observed for the rate of change of ε with temperature. The corresponding quantities for soft vulcanized rubber are -1.06×10^{-3} deg.$^{-1}$ and -2.6×10^{-3} deg.$^{-1}$, respectively.

The discrepancies observed with equations 5 and 6, applied to soft vulcanized rubber, are thought to be associated with its dipole moment, which has already been mentioned.

Note.—After this paper was completed, attention was called to the omission of several values which should have been included in this summary. Kemp[87], as the result of measurements on sol rubber hydrocarbon at 20° C., reported density values from 0.905 to 0.910 g.cm.$^{-3}$, the highest value being regarded as the most reliable. This value is equivalent to a density of 0.907 g.cm.$^{-3}$ at 25° C. The refractive index of sol hydrocarbon at 20° C. was found to range from 1.5214 to 1.5217. This range becomes 1.5196 to 1.5199 at 25° C. For hard rubber containing 32% sulfur, Kemp and Malm[88] reported a density of 1.163 g.cm.$^{-3}$ at 25° C.

Taylor, Herrmann and Kemp[89] reported values of the moisture diffusion constant for a number of materials. They define this as the rate at which water passes by diffusion through a section of unit area for unit vapor pressure gradient perpendicular to the section. For a certain soft vulcanized rubber compound, somewhat different from any considered here, the values ranged from 6.62×10^{-8} to 7.90×10^{-8} g.hr.$^{-1}$ cm.$^{-1}$ (mm. of mercury)$^{-1}$. For hard rubber containing 32% sulfur, the value 1.51×10^{-8} g.hr.$^{-1}$ cm.$^{-1}$ (mm. of mercury)$^{-1}$ was found.

X. SUMMARY AND CONCLUSIONS

A critical survey has been made of the values of 16 basic physical constants of rubber in the fields of mechanics, heat, optics and electricity. The value for each constant which seems most reliable has been indicated and, when necessary, has been corrected to the standard conditions of normal atmospheric pressure and a temperature of 25° C. The values have been given for rubber in four different forms: purified hydrocarbon, commercial raw rubber, soft vulcanized rubber containing 2% combined sulfur and hard rubber containing 32% sulfur.

The survey indicates that there are significant gaps in present knowledge of the fundamental properties of rubber. In some cases data are lacking, while

in many others the best values available are not of the accuracy required for present-day scientific and industrial work. This paper may therefore serve not only as a summary of selected values of the different constants, but also as a basis for the planning of future investigations.

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APPLICATION OF THERMODYNAMICS TO THE CHEMISTRY OF RUBBER *

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I. INTRODUCTION

The purpose of this paper is to show how thermodynamic data on rubber and related substances can be employed in studying and predicting their reactions. The method will be illustrated by the results of recent studies on rubber and isoprene made at the National Bureau of Standards. These results enable us to predict the conditions which favor the polymerization of isoprene to form rubber, and also the conditions which favor the reverse reaction, the thermal decomposition of rubber to give isoprene.

Rossini[1], in his review paper on "Modern Thermodynamics," makes the following statement: "The ultimate end of chemical thermodynamics may be said to be the evaluation of the free energy of formation, from the appropriate fundamental units of matter, of every substance in all possible states. . . ." Our chief object, then, for rubber is to obtain as accurately as possible the free energies of formation of rubber, sulfur, rubber-sulfur compounds and other forms of vulcanized rubber, isoprene and all other substances with which rubber reacts or from which it may be made.

II. THERMODYNAMIC PRINCIPLES

(1) Free Energy and the Equilibrium Constant

The term[2] free energy of a chemical reaction, symbolized in this paper by ΔF, refers to the change in free energy accompanying a chemical reaction (the formation of a substance from its elements being a special case) at constant temperature and pressure. This free energy, often called the thermodynamic potential of the reaction, is the criterion for determining the direction and extent to which the reaction will proceed. It can be used to calculate the equilibrium constant K of that reaction by means of the equation:

$$\Delta F^\circ = -RT \log_e K,$$

where R is the gas constant and T is the absolute temperature in degrees Kelvin. The free energy ΔF of the reaction in question may be calculated as the difference between the sum of the free energies of formation of the products of the reaction and the free energies of the reacting substances, the calculation being similar to that used for evaluating the heat of reaction ΔH, using the heats of formation of the products and the reactants.

When data are obtained on the free energy and the equilibrium constant for various temperatures and pressures, they serve to determine the optimum conditions at which the reaction will take place. This of course assumes that some catalyst can be found, if necessary, to bring the reaction to equilibrium. The catalyst does not significantly change the values of K or ΔF for the reaction unless it is present in large quantities. From the equation, $\Delta F^\circ = -RT \log_e K$, it can be seen that if $\Delta F = 0$, then $K = 1$. If ΔF is negative, $K > 1$; if ΔF is positive, $K < 1$.

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For a fair yield of product, K should be greater than 1, thus making ΔF negative; the greater the negative value of ΔF, the greater is the tendency for the reaction to occur. If ΔF is positive the reaction is not thermodynamically impossible, but would produce such a poor yield at those particular conditions of temperature and pressure that it would be impracticable, unless by some means the reaction products could be removed during the reaction, or some form of energy added[3].

Actually there are not a great number of chemical reactions which are known to attain equilibrium and which are so free from side reactions that the value of K may be obtained by direct measurement. This is especially true with reactions involving rubber. For this type of reaction the value of ΔF must be obtained by some indirect method. Of the various theoretically possible methods for obtaining the free energy of formation of the substances in question, the most promising seems to be by application of the equation $\Delta F = \Delta H - T\Delta S$, in which ΔH and ΔS are the heat of formation and the entropy of formation respectively.

(2) Heats of Formation

The heat of formation ΔH of a hydrocarbon from its elements is obtained from the measurement of the heat of combustion of the substance in question. This value, together with the values for the heats of combustion of solid carbon and gaseous hydrogen, is used to calculate the heat of formation of the substance in question from its elements.

In order to obtain sufficiently accurate values of ΔF, the heats of combustion must be determined with extreme accuracy. It has not been until recent years that improved technique and utilization of purer substances have provided data of sufficient accuracy to give good values for ΔF. These recently improved methods[1] give values of ΔH with uncertainties as low as 0.01 to 0.02% of the measured values. Kharasch[4] has developed a method for calculating the heats of combustion from the structure of the molecule, but this method, which gives results accurate only to about 1%, is not good enough for obtaining values for ΔF sufficiently accurate for present purposes.

(3) Entropies of Formation

The entropy of formation ΔS_T at any temperature T for a substance is obtained as the difference between the entropy of the substance at the temperature T and that of its elements at the same temperature. Determinations of the entropies of substances have recently been made by two different methods: (i) from heat capacity data, and (ii) from statistical calculations utilizing spectroscopic and other molecular data.

(i) *From Heat Capacity Data.*—In order to obtain the entropy of a substance at temperature T from heat capacity data, measurements on the latter must cover a range from T down to low temperatures, preferably as low as 10° or 20° K. The entropy of a substance at any temperature T is obtained from the equation:

$$S_T^O = S_O + \int_O^T C_p \frac{dT}{T} + \sum \frac{\Delta H_{tr}}{T_{tr}}$$

in which C_p is the heat capacity of the substance at constant pressure, ΔH_{tr} is the latent heat of any transition which the substance may undergo, such as melting, boiling, or crystalline rearrangement, and T_{tr} is the temperature of that transition. For the purpose of calculation of this entropy, all latent heat is assumed to be absorbed or liberated at a definite temperature and not over a range of tempera-

tures, and the heat capacity-temperature curves are extrapolated to this transition temperature from both sides. Then from the third law of thermodynamics, which states that all pure substances in a perfectly crystalline arrangement at the absolute zero of temperature have the same value of entropy[5], which for convenience is taken as zero, the entropies of the various substances at any temperature T are placed on a comparable basis since their measurements are made on the same scale.

Since C_p measurements cannot be made down to the absolute zero of temperature, an extrapolation of the curve must be made at the extreme low temperatures. This can be done by means of Debye's theoretical equation, which has been proved to be satisfactory at these low temperatures, *e. g.*, below 40° *K*. Tables[6] are available from which a $\beta\nu$ value (a value characteristic of a compound) can be obtained for the substance from the values of the heat capacity at the lowest temperatures at which these measurements were made. These tables can be used with confidence if the measurements are made as low as 20° or 30° *K*. These tables give also the entropy values at these low temperatures. These entropy values at 20° *K*. are of the order of only about 1% or less of the total values of the entropy at 298.2° *K*. (25° C.), thus introducing very little error by this extrapolation.

The increase in entropy of the substance from the lowest temperatures used in calorimetric measurements to the temperature T is obtained by measuring the area under the heat capacity curves between these temperatures, either with C_p plotted as a function of the natural logarithm of the absolute temperature, or with $\frac{C_p}{T}$ plotted as a function of the absolute temperature. This value, plus the entropy (from the Debye equation) of the substance at the temperature of the lowest part of the experimental curve, plus the entropies of all the transitions below temperature T obtained from $\frac{\Delta H_{tr}}{T_{tr}}$ gives the value of entropy $S_T{}^O$ of the substance at temperature T.

(ii) *From Statistical Calculations.*—Recently several theoretical investigators[7, 8, 9] have obtained entropies of some of the more simple or symmetrical compounds in the gaseous state by statistical calculations utilizing spectroscopic and other molecular data. This method is at present not applicable to solid substances such as rubber or to complex molecules like isoprene, and recourse must be had to the former method.

(4) Units of Energy

The commonly accepted temperature at which these thermodynamic data are reported is 25° C., which is about 298.2° *K*[10]. Units of heat energy are today defined in terms of electrical energy. The international joule is the quantity of heat generated per second by a current of 1 international ampere flowing through a resistance of 1 international ohm. However, since the calorie is a unit more popular in thermochemistry than the joule, even though less fundamental, a factor of 4.1833 international joules per calorie is used to obtain a "defined" calorie[1, 11]. All energy measurements reported in this paper are either in terms of this "defined" calorie, or the kilocalorie (abbreviated kcal.), which is equivalent to 1,000 of the former units. All calculations are made using 68.11 as the gram-molecular weight of isoprene. For convenient comparisons of thermochemical data of rubber with those of isoprene, all values for rubber are given per gram-mole of C_5H_8 (68.11 grams).

III. FORMS OF RUBBER

It is necessary that the rubber shall be in crystalline form for the determination of its entropy from the third law of thermodynamics. Since rubber exists in various forms, as has previously been determined from temperature-volume relationships[12], the sample must be put into and kept in the form desired for experimentation. The various forms are indicated in Fig. 1, which is a graph of the specific volume of rubber plotted as a function of the absolute temperature. At a temperature of about 200° *K.*, both the amorphous and crystalline forms of rubber exhibit an anomaly which is classed by Ehrenfest[13] as a transition of the second order. This anomaly is found not only in volume measurements, but also in measurements on heat capacity[14], dielectric constant[12] and stress-strain relationships[15]. Below 284° *K.* rubber may exist in both the amorphous and crystalline forms. At this temperature crystalline rubber undergoes a transition into the amorphous form, which is also shown by measurements on volume[12], light absorp-

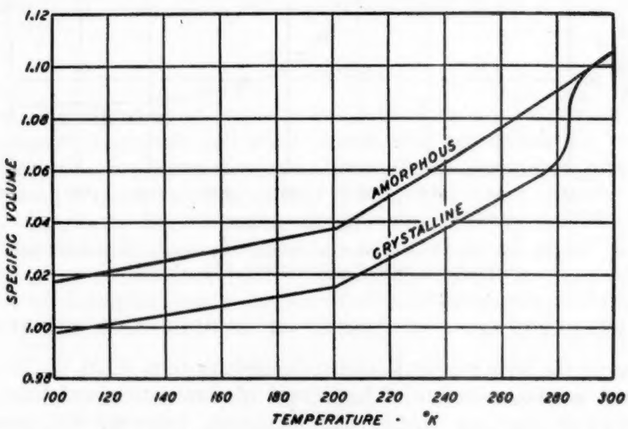

FIG. 1.—Relation between specific volume of rubber and temperature.

tion[16], hardness[16], x-ray diffraction[17, 18] and heat capacity[14]. The usual crystalline form of rubber does not exist above 284° *K.* under ordinary pressure conditions. However, there exists another form of frozen rubber which undergoes a similar transition at a few degrees above room temperature. The thermodynamic relationship of this form to the other forms of rubber is now being studied at the National Bureau of Standards.

The ordinary amorphous form of rubber can be brought into a crystalline form by keeping it in the temperature range from about 230° to 284° *K.* At all temperatures below the latter the crystalline form is thermodynamically the more stable, but evidently at the low temperatures, *e. g.*, below 230° *K.*, the viscosity of the rubber is so great that it hinders molecular orientation, thus causing the rubber to remain in its amorphous form.

The transformation of the amorphous form of rubber to the crystalline form is not rapid. The optimum temperature for conversion is in the vicinity of 250° *K.*, at which temperature the conversion is complete in a few hours. At 0° C. at least 10 days are required for complete transformation, as is shown in Fig. 2. Here the rate of the reaction is shown by measurements of the volume of the rubber in a dilatometer with alcohol as a confining liquid. In other dilatometers check mea-

surements were made using acetone, water and mercury as confining liquids. For heat capacity or other measurements, when the rubber sample is inside a container and cannot be identified as to its state by direct observation, it is cooled to a temperature near 250° *K*. and allowed to warm very slowly, *e. g.*, over a period of a day or two, to 0° C. and then kept at this latter temperature for several days before measurements are started.

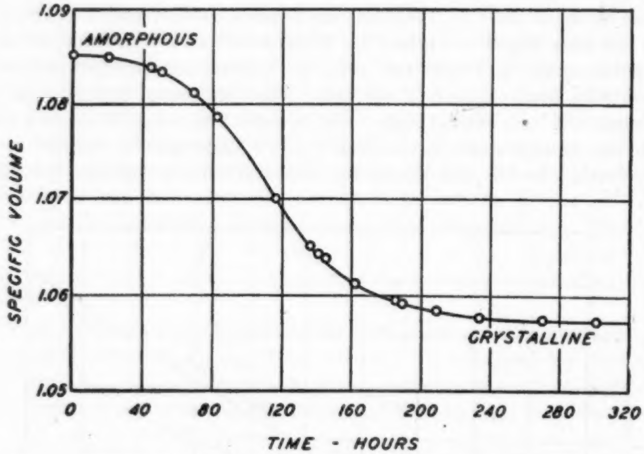

FIG. 2.—Decrease with time in specific volume of rubber as it changes from the amorphous to the crystalline form at 0° C.

IV. PREPARATION AND PURITY OF RUBBER AND ISOPRENE

In this paper the term rubber refers to the hydrocarbon $(C_5H_8)_n$. In preparing samples used in measurements of both heat of combustion and heat capacity, the impurities of the raw rubber were removed, following the procedure of McPherson[19]. In this method crude rubber or latex is digested with water at about 190° C. to hydrolyze the proteins. Extractions are then made with water and alcohol to remove the products of hydrolysis, resins and other impurities, leaving less than 0.5% of non-hydrocarbon components.

The isoprene samples used in the investigations of heat capacity and heat of combustion were prepared by cracking dipentene vapors, and then purified by successive distillations through an efficient fractionating column[20]. The samples were tested immediately after distillation. The difference between the boiling and condensation temperatures, as determined by the method of Swietoslawski[21], was found to be 0.002 C. From the time-temperature freezing curve, the amount of liquid-soluble, solid-insoluble impurities may be calculated by the method of White[22] to be of the order of one mole-per cent. Immediately after final distillation, the samples were hermetically sealed in containers for measurements of heat capacity and heat of combustion in order to keep oxidation and polymerization at a minimum. The samples were exposed to the atmosphere during transfer of the isoprene to the containers used in the determination of the heat of combustion, and there were indications that some moisture was absorbed. Corrections for the presence of this moisture were made by Jessup[23] in his determination of the heat of combustion.

V. HEATS OF COMBUSTION

(1) Rubber

The heat of combustion of rubber has been reported by various investigators[24, 25, 26, 27, 28, 29, 30, 31, 54], but the careful work of Jessup and Cummings[28] was the only one to include measurements on rubber purified in the same manner as that used in the measurements of heat capacity. Their value for steam-purified rubber at 30° C. is 45239 ± 90 international joules per gram, or 736.6 ± 1.5 kcal. per mole of C_5H_8. Using 0.452 cal. per gram per degree for the average specific heat of rubber[14] between 25° and 30° C., 8.8 cal. per mole per degree for carbon dioxide[32], 7.0 cal. per mole per degree for oxygen[32], and 18.0 cal. per mole per degree for water[33], the heat of combustion of the rubber hydrocarbon at 25° C. is calculated to be 736.7 ± 1.5 kcal. per mole of C_5H_8. Using the heats of formation at 25° C. of gaseous carbon dioxide as -94.24 ± 0.10 kcal. per mole[34, 35], and of liquid water -68.313 ± 0.010 kcal. per mole[36], the heat of formation of rubber hydrocarbon from its elements, $\Delta H_{298.2}$, is calculated to be -7.7 ± 1.6 kcal. per mole of C_5H_8[37].

(2) Isoprene

The heat of combustion of isoprene was determined by Lebedev, Chochlovkin and Kalacheva[38], but their individual values were not sufficiently consistent to warrant their use for present purposes. Jessup[23] has determined this value very precisely, using a bomb calorimeter and a sample of liquid isoprene purified as previously described. He obtained a value corresponding to 3156.8 ± 1.6 international kilojoules per mole (754.62 ± 0.38 kcal. per mole) at 25° C. and at a constant pressure of one atmosphere. Calculations similar to those described for rubber give for liquid isoprene a value of 10.17 ± 0.63 kcal. per mole for $\Delta H_{298.2}$.

VI. HEAT CAPACITIES

(1) Rubber

The heat capacity of rubber has been measured by several investigators[14, 30, 39, 40, 41, 42], but only the work done at the National Bureau of Standards[14] included temperatures low enough for accurate extrapolation with the Debye formula. A reproduction of this heat capacity curve for rubber is given in Fig. 3. For the sake of comparison with a similar curve for isoprene, the values are given in calories per mole of C_5H_8. Heat capacity measurements were made on both the crystalline and amorphous forms of rubber. It can be seen from the curve that within the experimental error the heat capacity values for the crystalline and the amorphous forms of rubber are the same at the lower temperatures, but as the temperature rises the crystalline form assumes the lower value. At a temperature of about 200° *K*. there appears the transition of the second order, which takes place in both the amorphous and the crystalline forms of rubber. The crystalline form of rubber undergoes a transition of the first order, in which the crystals melt; the center of the range in which this transition occurs is about 284° *K*. The heat of melting of the rubber crystals was determined during the process of measuring heat capacities and was found to be 272 cal. per mole of C_5H_8, which is identical with the value reported by Ruhemann and Simon[42], obtained in a similar manner.

(2) Isoprene

All measurements of the heat capacity of isoprene[43] were made within 2 weeks after its purification, so that the sample had very little time to polymerize or oxidize. The values obtained for isoprene are also reproduced in Fig. 3. Its heat capacity is much higher than that of an equivalent weight of rubber hydrocarbon. It exhibits no transition of the second order as does the rubber at about 200° *K*. Crystalline isoprene, however, melts at a much lower temperature, 126.4 *K*., and absorbs 1155±4 cal. per mole of heat in the process.

The broken lines from 0° to 50° *K*. are the Debye theoretical curves for rubber and isoprene. They agree very well with the experimental curves at the lower

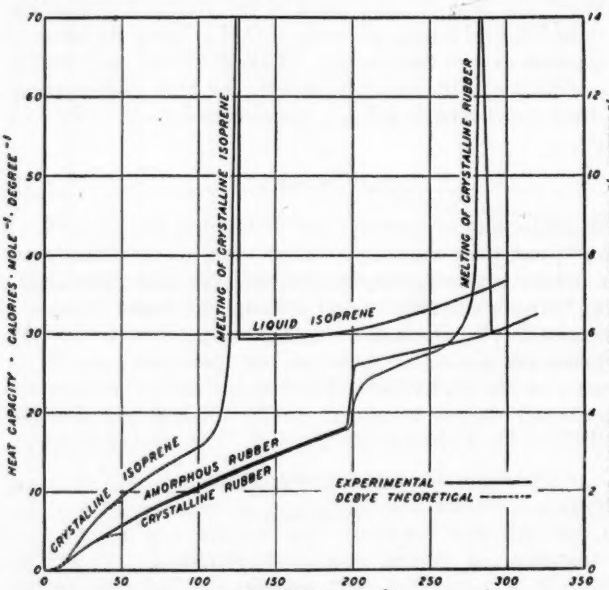

Fig. 3.—Relation between heat capacity and temperature for isoprene and rubber hydrocarbon.

temperatures. In order to obtain these theoretical curves, a $\beta\nu$ value of 127 was chosen for isoprene and a $\beta\nu$ value of 110 for rubber hydrocarbon. This value of 110 for rubber gives a theoretical curve which is in better agreement with the experimental curve than is the previously chosen value[14] of 120. The effect on the entropy, however, is to decrease the previously determined value by only 0.015 cal. per (mole of C_5H_8) per degree, which is considerably less than the probable error of the total entropy at 298.2° *K*.

VII. ENTROPIES OF RUBBER AND ISOPRENE

The entropies of isoprene and crystalline rubber hydrocarbon, as calculated from the heat capacity data, are 54.8±0.2 and 30.6±0.2 cal. per mole per degree, respectively. The entropy of the amorphous form of rubber is given as 0.28 unit higher at the absolute zero than that for the crystalline form. This difference is but very little greater than the probable error. Parks[44] believes that the rubber may have been partially amorphous because of its low heat of fusion and because

the transition of the second order also takes place in the crystalline form. However, the value for the entropy of the crystalline form would not be changed to an extent which would significantly influence the calculated value of the free energy of formation of the rubber.

Parks and Huffman[45] have given equations for the estimation of entropies of organic compounds from their structural formulas. From these equations the entropy of isoprene is predicted to be 53.6 cal. per mole per degree for the liquid form at 25° C. For rubber hydrocarbon, assuming a long-chain molecule having one CH_3 branch chain and one double bond per C_5H_8 unit, the entropy is predicted to be 31.3 cal. per (mole of C_5H_8) per degree. These values differ from the experimental values by -1.2 and $+0.7$ units for isoprene and rubber respectively. These differences are so small that the use of these predicted values in the calculation of the free energies of formation of these compounds would not have affected the final results by amounts as great as the corresponding probable errors, which arise for the most part from the errors in measuring the heats of combustion. This, however, could not have been previously assumed, since the equations given by Parks and Huffman are not claimed to give results of very great accuracy. These equations were developed from data on a limited number of the simpler organic compounds, and in many cases involved extrapolation of the entropy from about 90° *K*. to the absolute zero. For a substance having a molecular structure as complicated as that of rubber the estimated value is remarkably close to the experimental value.

Using 1.36 ± 0.03 cal. per mole per degree and 31.23 ± 0.00 cal. per mole per degree as the entropies of carbon (graphite)[46] and hydrogen[47] respectively at 25° C., the entropy of isoprene $\Delta S_{298.2}$ is calculated to be -76.92 ± 0.25 cal. per mole per degree. Likewise for the crystalline form of rubber hydrocarbon, $\Delta S_{298.2}$ is -101.12 ± 0.25 cal. per (mole of C_5H_8) per degree.

VIII. FREE ENERGIES OF RUBBER AND ISOPRENE

From the heats of formation and the entropies of formation of rubber hydrocarbon and isoprene from their elements, their free energies of formation, or thermodynamic potentials, are calculated. For rubber:

$$\begin{aligned}\Delta F^\circ_{298.2} &= (-7.7 \pm 1.6) - 298.2(-0.10112 \pm 0.00025)\\ &= 22.5 \pm 1.6 \text{ kcal. per mole of } C_5H_8.\end{aligned}$$

Likewise, for isoprene:

$$\begin{aligned}\Delta F^\circ_{298.2} &= (10.17 \pm 0.63) - 298.2(-0.07692 \pm 0.00025)\\ &= 33.11 \pm 0.68 \text{ kcal. per mole.}\end{aligned}$$

IX. THERMODYNAMIC RELATIONSHIP BETWEEN ISOPRENE AND RUBBER

(1) Free Energy under Standard Conditions

For the free energy change during the chemical reaction for the polymerization of isoprene to form rubber at 25° C. and at one atmosphere pressure:

$$C_5H_8 \text{ (liq., 1 atm.)} \rightleftharpoons \frac{1}{n}(C_5H_8)_n \text{ (solid)}$$

the heats of combustion and the entropies of the elements carbon and hydrogen cancel each other and the equation for the free energy of the reaction becomes:

$$\begin{aligned}\Delta F^\circ_{298.2} &= [(736.7 \pm 1.5) - (754.62 \pm 0.38)] - T[(0.0306 \pm 0.0002) - (0.0548 \pm 0.0002)]\\ &= (-17.9 \pm 1.6) - 298.2(-0.0242 \pm 0.0003).\end{aligned}$$

In the latter equation the terms in the parentheses are the heat of the reaction $\Delta H_{298.2}$ and the entropy change during the reaction $\Delta S_{298.2}$, respectively. The equation gives -10.7 ± 1.6 kcal. per mole of C_5H_8 as the free energy change $\Delta F^{\circ}_{298.2}$ of the reaction.

(2) Equilibrium Constant under Standard Conditions

From this free energy of the reaction, the equilibrium constant is calculated from the equation:

$$\Delta F^{\circ} = -RT \log_e K$$

$$\log_e K = \frac{10{,}700}{1.987 \times 298.2}$$

from which K is approximately 7×10^7.

This large value of K indicates that the reaction in question if brought into equilibrium at room temperature would be practically complete in the direction of the rubber. The thermodynamic potential is so great in that direction that with the use of a suitable catalyst no improvement need be sought so far as changes of temperature and pressure are concerned.

(3) Effect of Pressure on the Free Energy

According to the principle of Le Chatelier and from the thermodynamic formula:

$$\left(\frac{\partial \Delta F}{\partial P}\right)_T = \Delta V,$$

a change in the external pressure will change the free energy of the reaction if it is accompanied by a volume change ΔV. There is a decrease in volume when isoprene polymerizes to form rubber. The density of the former at 25° C. is 0.6754 g. per cc.[20] and of the latter is 0.9060 g. per cc.[19] at the same temperature. For one mole of isoprene in this reaction at 25° C., ΔV is then calculated to be -25.66 cc.

Neglecting the compressibility of both rubber and isoprene, the free energy equation for the reaction in kcal. per mole of C_5H_8 at a constant temperature of 25° C. is $\Delta F_{298.2} = -10.7 - 0.0006P$, where P is the pressure in atmospheres. This equation indicates that the application of pressure has a slight effect on the equilibrium of the reaction. Actually, the effect must be less than the above equation indicates, since Conant and Peterson[48] have shown that isoprene is much more compressible than rubber. However, the effect is present, since their experiments and also some by Conant and Tongberg[49] have shown that an increased yield of a rubber-like substance is obtained if great external pressure is applied.

(4) Effect of Temperature on the Free Energy

At the temperature for which the previous calculations have been made, isoprene is in the liquid state but within only a few degrees of its normal boiling point[20] of 34.076° C. In the calculation of the free energy of the reaction for temperatures at which the isoprene is in the gaseous state, it is desirable to determine $\Delta F_{307.3}$, the free energy change at the normal boiling point.

Extrapolation of the heat capacity curve of the isoprene to its boiling point gives an average value of 36.45 cal. per mole per degree from 298.2° to 307.3° K. The entropy increase for the liquid isoprene between these two temperatures is calculated from the equation:

$$S_{307.3} - S_{298.2} = \int_{298.2}^{307.3} \left(\frac{C_p}{T}\right) dT$$

to be 1.1 cal. per mole per degree (0.0011 kcal. per mole per degree). The increase in entropy of rubber hydrocarbon between these temperatures, calculated from its heat capacity, is 0.0009 kcal. per (mole of C_5H_8) per degree.

The heats of combustion of rubber and isoprene at 307.3 *K*. are 736.4±1.5 kcal. per mole of C_5H_8 and 754.36±0.38 kcal. per mole, respectively. The heats of combustion at 307.3° *K*. are lower than those at 298.2° *K*. by 0.31 and 0.26 kcal. per mole of C_5H_8 for rubber and isoprene, respectively. Since an increase in the temperature of the combustion reaction from 298.2° to 307.3° *K*. lowers the heat of combustion for rubber by 0.05 kcal. per mole of C_5H_8 more than for an equivalent amount of liquid isoprene, the heat of the polymerization reaction $-\Delta H$ is increased in numerical value by this same amount. For the same change in temperature, the entropy of liquid isoprene is increased by 0.0002 kcal. per (mole of C_5H_8) per degree more than that of the equivalent amount of rubber, which causes the change in entropy of the reaction ΔS to be increased by 0.0002 unit. Thus the free energy of the polymerization reaction at 307.3° *K*. is:

$$\begin{aligned}\Delta F^\circ_{307.3} &= (736.4-754.36)-307.3(0.0315-0.0559)\\ &= -10.5\pm 1.6 \text{ kcal. per mole of } C_5H_8.\end{aligned}$$

Since the free energy change ΔF is zero for the reaction:

$$C_5H_8 \text{ (liq., 1 atm.)} \rightleftharpoons C_5H_8 \text{ (gas, 1 atm.)}$$

the above equation for the free energy of the polymerization reaction at the boiling point of isoprene, 307.3° *K*., is true for isoprene in either the liquid or gaseous state.

From the heat capacities from 0° to 300° C. of a number of paraffin and olefin hydrocarbons, given by Beeck[50], a fairly reliable estimate of the heat capacity values for gaseous isoprene may be obtained. The slopes of the heat capacity-temperature curves, $\frac{dC_p}{dT}$, are the same for the paraffin hydrocarbons, C_4H_{10}, C_5H_{12}, and C_6H_{14}, the value being 0.00097 cal. per gram per degree^2. No data for the 5-carbon olefins are given, but not only are the heat capacity-temperature curves for C_3H_6 and C_4H_8 identical in slope with those for the three previously mentioned paraffins, but also the C_p values themselves are identical with those for C_5H_{12} when compared on the same weight basis. The equation obtained from the data is $C_p=0.070+0.00097T$ in cal. per gram per degree. Assuming the same equation to hold true for gaseous isoprene, the equation becomes:

$$C_p=4.8+0.066T$$

in cal. per mole per degree.

The only value found in the literature for the heat capacity of rubber at elevated temperatures is one calculated from the change in heat content of the rubber between 25° and 175° C.[30]. This gives a mean heat capacity of 35.4 cal. per (mole of C_5H_8) per degree at 100° C. (373° *K*.). The curve in Fig. 3 is extrapolated to higher temperatures by drawing a straight line from the point of the highest temperature in the curve (320° *K*.) through the previously mentioned point at 373° *K*. The values of the heat capacity from this curve agree with the experimental values for the amorphous form of rubber at the temperatures immediately above the transition of the second order (200° *K*.). The equation of the extrapolated curve is:

$$C_p=14.5+0.056T$$

where C_p is in cal. per (mole of C_5H_8) per degree.

The difference between the heat capacities of rubber and gaseous isoprene at temperatures above 300° K. is then given by the equation:

$$\Delta C_p = (0.0097) + (-0.000010)T$$

in kcal. per mole per degree. The constants in the parentheses will in the following equations be designated as $\Delta\Gamma_0$ and $\Delta\Gamma_1$ respectively.

For any temperature T, the free energy change for the reaction ΔF_T may be calculated from the following equation:

$$\Delta F_T = \Delta H_T - T\Delta S_T$$

$$\Delta H_T = \Delta H_s + \Delta\Gamma_0 \int_{T_s}^{T} dT + \Delta\Gamma_1 \int_{T_s}^{T} T\,dT$$

$$\Delta S_T = \Delta S_s + \Delta\Gamma_0 \int_{T_s}^{T} \frac{dT}{T} + \Delta\Gamma_1 \int_{T_s}^{T} dT$$

Substituting the terms obtained from the integration of the last two equations in the preceding one, the following equation is obtained:

$$\Delta F_T = A + BT + CT^2 + DT \log_e T$$

in which

$$A = \Delta F_s + T_s\Delta S_s - \Delta\Gamma_0 T_s - \tfrac{1}{2}\Delta\Gamma_1 T_s^2$$
$$B = \Delta\Gamma_0 + \Delta\Gamma_0 \log_e T_s - \Delta S_s + \Delta\Gamma_1 T_s$$
$$C = -\tfrac{1}{2}\Delta\Gamma_1$$
$$D = -\Delta\Gamma_0.$$

Taking $T_s = 307.3°$ K., the normal boiling point of isoprene, and evaluating the constants A, B, C, and D, the free energy of the polymerization of gaseous isoprene in kcal. per mole at temperature T and at a pressure of one atmosphere is given by the following equation:

$$\Delta F_T° = -20.51 + 0.0866T + 0.000005T^2 - 0.0097T \log_e T.$$

This equation, which is represented by a graph shown in Fig. 4, indicates that there is less tendency for polymerization to proceed at the higher temperatures. The equilibrium constant, therefore, decreases with a rise in temperature, becoming

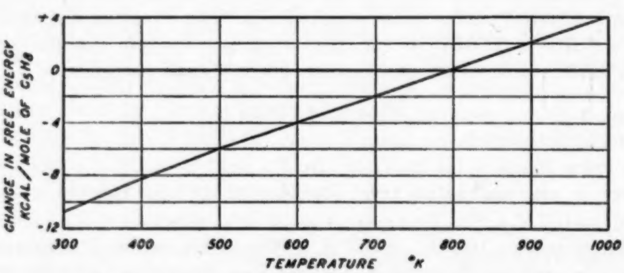

FIG. 4.—Relation between the free energy change and temperature in the polymerization reaction of isoprene to form rubber.

unity when ΔF is zero at about 800° K. Above this temperature isoprene is thermodynamically the more stable, and the reaction tends to proceed more in the direction of isoprene. This is in accord with experimental results of several investigators who have prepared isoprene by destructive distillation of rubber[51, 52, 53].

X. SUMMARY AND CONCLUSIONS

Various thermodynamic functions for purified rubber, isoprene and the reaction of polymerization of isoprene are calculated from data on the heats of combustion and the heat capacities of these compounds. For the polymerization reaction of isoprene to form rubber:

$$C_5H_8 \rightleftarrows \frac{1}{n}(C_5H_8)_n$$

at 25° C. and at one atmosphere pressure, the heat of reation $\Delta H_{298.2}$ is -17.9 ± 1.5 kcal. per mole; the change in entropy $\Delta S_{298.2}$ is -0.0242 ± 0.0003 kcal. per mole per degree; and the change in free energy $\Delta F°_{298.2}$ is -10.7 ± 1.6 kcal. per mole. The equilibrium constant for the reaction under the same conditions of temperature and pressure, calculated from the free energy, is approximately 7×10^7.

At constant temperature, the free energy of the reaction varies with a change in the external pressure. Neglecting a difference between the compressibilities of liquid isoprene and rubber, this free energy change in kcal. per mole can be calculated from the equation:

$$\Delta F_{298.2} = -10.7 - 0.0006P$$

where P is the pressure in atmospheres. For temperatures at which the isoprene is in the gaseous state, the free energy difference will be increased to a much greater extent by the application of pressure.

At a constant pressure of one atmosphere the free energy of the polymerization of the gaseous isoprene may be calculated in kcal. per mole from the equation:

$$\Delta F_T° = -20.51 + 0.0866T + 0.000005T^2 - 0.0097T \log_e T.$$

An increase in temperature causes an increase in the free energy of the reaction, the value becoming zero at about 800° K. and positive above this temperature.

This free energy equation indicates that below 800° K. rubber is thermodynamically more stable than isoprene, and that the reaction will proceed in the direction which favors the formation of rubber. At any temperature below 600° or 700° K. the free energy difference between these two compounds is great enough to indicate that the reaction will go practically to completion. Above 800° K. the tendency of the driving force is in the opposite direction, favoring depolymerization. The free energy of reaction determines suitable or optimum conditions under which the reaction will take place, but says nothing about the rate at which it will proceed. Evaluation of the free energies of formation of other substances with which rubber may react or from which it may be made will permit the prediction of the conditions for other chemical reactions. Then, with these conditions in view, searches can be made for catalysts which will bring the desired reactions into equilibrium.

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MASTICATION OF RUBBER

A STUDY OF SOME OF THE OXIDATION PROCESSES INVOLVED *

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INTRODUCTION

Oxygen plays an essential role in the mastication of rubber[1,2], but very little is known of the details of the reactions which are involved. It has been observed[2] that breakdown of rubber on a cold mill is accompanied by a luminous discharge and the formation of peroxides, and that each of these effects has a negative temperature coefficient. This suggests that mill mastication involves the activation of the long rubber molecules by mechanical deformations and also an activation of oxygen in the air by the electric charges, the activated rubber and the activated oxygen probably combining to form intermediate products which later give off volatile peroxides.

Rubber may be broken down also by the so-called heat-softening or vacuum-softening processes[3], in which it is heated in thin sheets in air for several hours to make it soft and plastic. Oxygen is responsible for this breakdown just as it is in mastication, but it must act by a different mechanism, for there is no appreciable distortion of the rubber during heat softening, and the temperature coefficient of this reaction is positive. Here the oxidation mechanism probably involves an activation of the rubber molecules by their thermal kinetic energy, just as in other slow combustion reactions. If the temperature is raised sufficiently high, the thermal agitation will, of course, become so violent that the molecules will decompose or "crack" even in the absence of oxygen to give products which may range from thick, viscous liquids to low-boiling compounds such as dipentene. Recently published data[4] show that mastication at temperatures of about 300° or 400° F. has a positive temperature coefficient, indicating that under some conditions thermal oxidation may play a part in breakdown during mastication.

Rubber "softeners" such as fatty acids, zinc laurate, rosin, mineral oils, phenylhydrazine and thiophenols are commonly used to increase the plasticity of rubber, and it is often assumed that they act through some lubrication, swelling, or "peptizing" action on rubber, although the evidence for these views is meagre or entirely lacking.

To learn more about the mechanism of some of these reactions, rubber containing various chemicals was masticated in a small internal mixer at a wide range of temperatures and in atmospheres of various gases. Plasticity measurements of the processed rubber showed that at least two types of reaction are possible during mastication, and that these reactions are affected very differently by changes in the oxygen concentration of the atmosphere and by addition of mastication accelerators.

EXPERIMENTS

The rubber was masticated in 700-gram batches in a Schiller internal mixer fitted with individually driven Banbury-type blades which ran 30 and 45 r.p.m.,

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respectively. The mixer was equipped with a recording watt-meter for power consumption and a thermocouple and recording potentiometer to show the rubber temperature. The temperature of the rubber was controlled by manual adjustments of the steam or water circulating through the jacket of the mixer. A special thermocouple was designed by Hahn of this laboratory for measuring the rubber temperatures in the mixer. The hot junction was brazed to a small bead of phosphor-bronze attached, in turn, to the bottom surface of a piece of Bakelite inserted in the end of a steel tube which, during operation of the mixer, extended down from the lid into the rubber. The heat lag with this device was very small, since the phosphor-bronze button at the hot junction was in direct contact with the rubber. The low thermal conductivity of the Bakelite backing reduced heat losses to the lid, and the small loss that did exist was, in part at least, compensated by the effect of friction of rubber on the thermocouple. The action of the recorder indicated that the time lag of the couple was of the order of half a minute, and at equilibrium the thermocouple probably indicated within 5° of the true rubber temperature. The rubber was kept within ±5° of the desired value throughout most of the test except for those batches run near the upper or lower limits (330° and 165° F. respectively) of the temperature range, where the deviations were somewhat larger.

The recording watt-meter indicated the power needed to turn the mixer at all stages of the mastication process. Any unusual condition of the batch, such as crumbling on the addition of pigments, immediately affected the power consumption, and with normal batches this reading also furnished a quick but very rough indication of the plasticity of the rubber at the operating temperature. The batch on removal from the mixer was given two passes through a warm mill, the rolls of which were set to give a thin sheet on the first pass, and a slab about $\frac{5}{8}$ in. thick on the second pass.

The extent of breakdown was determined by measuring the plasticity of the rubber with the Goodrich plastometer[5], usually at a temperature of either 158° or 212° F. (70° or 100° C.). This type of plastometer was particularly useful in these tests because it measures both the softness and retentivity of the rubber, as well as the combination of these in the final plasticity result. It was found, for example, that chemicals such as nitroso compounds or nitrites produced in rubber a different softness-retentivity relation from that of normally masticated crude rubber of the same plasticity. These differences clearly indicate that the chemicals do something besides accelerate the normal mastication process.

The absolute value of the rate of breakdown in the internal mixer depends to a high degree on mechanical factors, such as the speed of the blades, the clearance between blades and shell and the shape of the wiping edge of the blade; hence these factors must be kept constant during any one series of tests. When the rubber was masticated in different atmospheres, the desired gases were led through holes in the lid and the gas in the machine was kept at a positive pressure of a few inches of water. Chemicals were added to the rubber from a reservoir, which was also flushed out with the gas used in the mixer. This arrangement made it unnecessary to remove the lid or interrupt the mixing. No precautions were taken to purify the gases. When the rubber was masticated in air the hole in the lid was merely left open.

(1) Effect of Temperature on Rate of Breakdown in Air

(a) Different Rubbers.

The first series of tests showed the effect of mastication temperature on rate of breakdown of smoked sheet masticated for 20-minute periods in the internal

mixer in air (Fig. 1). All plasticity measurements in this series were made at 212° F.

When crude smoked sheet having a plasticity of 3.7 was put in the mixer and masticated at different temperatures the results shown in Curve A were obtained. Mastication at 180° F. raised the plasticity from 3.7 to 22, or an increase of about 18 points. When the mastication temperature was raised the rate of breakdown decreased, samples masticated at 240° having a final plasticity of only 9. The change in plasticity in this case was only a little over 5, or about one-fourth as great as at 180° F. When the mastication temperature was raised above 240° the rate of breakdown again increased, the rate being about as rapid at 330° as at 180° F. Curve B shows that the change in rate of breakdown with temperature for rubber which had been previously mill-masticated in a 250-lb. batch on an 84-inch mill to a plasticity of 11.3 was of the same type as that obtained with crude rubber. Curve C shows that similar results were obtained with smoked sheet previously broken down in a Gordon Plasticator to a plasticity of 14.2.

Most other rubbers exhibit this same type of change in the rate of mastication with temperature, but in some cases the minimum rate of breakdown may come at higher or lower temperatures. The data for different rubbers shown in Table I were obtained after the mixer had been taken down and the blades remodelled to

TABLE I

	Plasticity at 212° F.				
		Masticated at:			
Kind of rubber	Initial rubber	160° F.	180° F.	240° F.	320° F.
Gordon plasticated smoked sheet.....	15.8	66.7	—	29.3	62.7
Crude pale crepe....................	2.7	—	23.9	12.6	49.0
Acetone-extracted pale crepe.........	4.6	54.0	—	19.1	71.4
L.S. No. 1...........................	2.0	—	20.0	9.5	16.8

reduce the clearance between the blades and the shell, so the rate of breakdown at all temperatures was faster than it was for the previous series. However, it is seen that the rate of breakdown of smoked sheet, pale crepe, and L. S. (sprayed latex) rubbers is slower at 240° than at the higher or lower temperatures.

It appears from these tests that mastication in this internal mixer at temperatures below about 240° F. resembles mastication on a mill, where, due to conduction and radiation, the temperature rarely rises much above 200° F. In both cases rubber presumably is activated by mechanical distortions. At temperatures above 240° in the mixer another type of breakdown becomes important. The present data suggest, but do not prove, that this high-temperature reaction involves a thermal activation and oxidation of the molecules.

(*b*) *Rubber Containing Chemicals.*

"Softeners" of unvulcanized rubber may be classified roughly into three groups in the order of their activity. The first, least active group, may be typified by mineral oil. It must be used in quantities of about 5 to 20% to produce an appreciable change in plasticity, so one would expect materials of this group to act largely by their purely physical effect as diluents of the rubber.

The second group, of intermediate activity, includes materials such as fat acids and their zinc soaps. They usually show reasonable activity at concentrations of about 3 to 6%, and they may act in part as diluents and in part by other (chemical?) mechanisms. The third group includes the newer chemical softeners such as phenylhydrazines and thiophenols, which are very active at concentrations of 0.1% to 0.25%. These probably act by some chemical mechanism.

A number of these softeners and other chemicals were milled into rubber at a range of temperatures to see if they had the same effect on the low and the high-temperature reactions. Masticated smoked sheet with an initial plasticity of $6.3 \pm .5$ at 158° F. was put into the mixer and masticated for 3 minutes to warm up; then the chemical was added and the mastication continued for 17 minutes more. The results are shown in Table II.

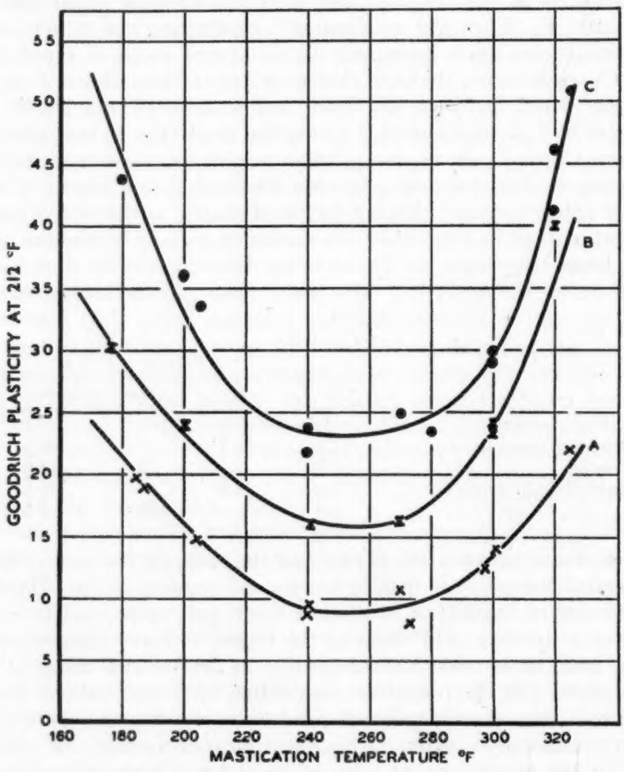

FIG. 1.—Effect of temperature on the rate of breakdown of smoked sheet. A—Crude rubber; B—Mill-masticated rubber; C—Gordon-plasticated rubber.

It is significant that in most cases the effect of softeners on the rate of mastication is relatively small compared with the effect of temperature. There are a few discrepancies in the Table, probably due to differences in the activity of the chemicals or the rubbers used in the different series, or to occasional trouble with the temperature control, but in general the results are reliable to about ±10%. Lauric and oleic acids seem to accelerate the low-temperature reaction more than the high-temperature reaction, but zinc laurate seems to have its greatest effect at high temperatures. 0.2% butylamine or 0.2% *p*-nitrosodimethylaniline is as good as 1 or 2% zinc laurate as softeners at 275° or below, but at 325° F. the *p*-nitrosodimethylaniline is a stiffener. It produces also an abnormal relation between the softness and retentivity factors.

Ester gum, and strangely enough, also Perhydrol (30% hydrogen peroxide) have little, if any, effect on the rate of mastication. Phenylhydrazine, on the contrary, is such a powerful softener that concentrations of only 0.2 per cent. are needed to increase the rate of breakdown from 6- to 10-fold at temperatures from about 240° to 275° F., but it produces smaller increase in the rate of breakdown at temperatures above and below this range. The differences in the results with 0.2% phenylhydrazine in the two series of tests may have been due to a difference in the purity of the two samples used, or possibly to differences in the rubber. On the basis of other tests the results of Series 2 seem to be the more reliable.

TABLE II.

EFFECT OF TEMPERATURE ON RATE OF BREAKDOWN OF RUBBER CONTAINING VARIOUS CHEMICALS

Chemical added	Amount (%)	Plasticity at 158° F. when masticated at: 160° F.	180° F.	240° F.	275° F.	300° F.	325° F.
Series 1:							
None	—	25.0	—	10.8 ± 1.2	11.0	14.7	26.5 ± 4
Zinc laurate	3.0	27.0	—	18.5	—	—	50 ± 6
Oleic acid	3.0	40.0	—	14.0	—	—	36.7
Lauric acid	3.0	38.9	—	13.4	—	—	35.0
Ester gum	3.0	29.6	—	14.1	—	—	28.7
Rosin	1.0	—	—	12.8	11.4	17.2	41.4
Rosin	3.0	—	—	13.6	13.5	23.0	43.6
Series 2:							
None	—	24.8	21.0	8.2	8.7	18.1	20.2
Perhydrol	0.2	—	20.8	9.2	10.5	13.5	19.2
Zinc laurate	1.0	—	24.5	8.3	10.9	22.0	30.2
Butylamine	0.2	—	24.3	12.5	13.1	16.0	19.1
p-Nitrosodimethylaniline	0.2	—	22.8	13.7	14.7	14.2	12.0
Phenylhydrazine	0.2	—	28.3	29.6	45.4	39.7	27.6
Series 3:							
None	—	—	—	9.4	8.6	13.5	22.6
Phenylhydrazine	0.2	—	—	36.5	26.4	25.1	27.2
		170° F.				320° F.	
Series 4: (Mixer remodelled):							
None	—	35.3				62.0	
Age-Rite Powder (phenyl-β-naphthylamine)	2.0	35.8				41.4	
Age-Rite Resin	2.0	37.2				32.5	
Captax (mercaptobenzothiazole)	2.0	36.8				85.0	
Captax (mercaptobenzothiazole)	0.2	40.4				81.7	

The data of Series 4 were taken after the mixer had been dismantled and repaired, and the clearance between the blades and shell reduced. Gordon-plasticated smoked sheet with a plasticity of 8.1 ± 0.5 was used. These tests and others not listed show that most age-resisters have little effect on the low-temperature breakdown, but they appreciably retard the breakdown at high temperatures. However, diamines tend to stiffen rubber at all temperatures. Captax and Altax (benzothiazyl disulfide) and the zinc salt of Captax are almost inert at low temperatures, but they considerably accelerate the high-temperature reaction.

The peculiar behavior of certain nitroso compounds[6] in softening rubber under some conditions and stiffening it under others made it worth while to study the effects of these compounds on softness and retentivity as well as on plasticity. The results are shown in Table III, where S, the softness, is a measure of the ease of deformation, R is retentivity, or percentage deformation retained, and

TABLE III

EFFECT OF CHEMICALS ON RATE OF MASTICATION

Chemical added	Plasticity data at 158° F. when masticated at: 165° F. S.	R.	P.	240° F. S.	R.	P.	320° F. S.	R.	P.
None	37.0	59.3	22.2	22.3	42.3	9.5	35.1	57.6	20.3
Nitric acid	30.7	43.2	13.3	25.6	44.8	11.4	35.9	53.3	19.1
Nitrosobenzene	—	—	[a]	15.5	31.0	4.8	24.1	25.8	6.1
p-Nitrosodiphenylamine	42.5	49.3	20.6	32.1	34.5	11.1	40.7	43.5	17.7
n-Butyl nitrite	23.5	27.4	6.5	24.1	26.9	6.5	—	—	[b]
Azoxybenzene	46.4	70.0	32.5	21.0	44.8	9.4	50.2	72.8	36.6

[a] Batch was so stiff it would not knit together in the mixer.
[b] n-Butyl nitrite was not tested at 320° F. because of possible health hazards from the vapors.

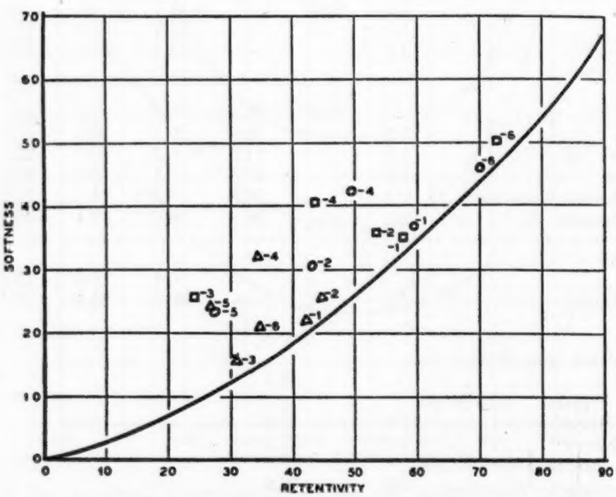

FIG. 2. Softness-retentivity relations of rubbers milled with various chemicals. Mastication temperature: ○ 165° F.; Δ 240° F.; □ 320° F.
1 Control—no chemical added; 2 Nitric acid; 3 Nitrosobenzene; 4 p-Nitrosodiphenylamine; 5 n-Butyl nitrite; 6 Azoxybenzene.

the product of these, divided by 100, is the plasticity, P. The mastication procedure was the same as for the data shown in Table II.

Nitric acid has very little effect on softness, retentivity or plasticity at 240° or 320° F., but it slightly reduced these factors at 165° F. Nitrosobenzene and butyl nitrite are powerful stiffeners at all temperatures, while azoxybenzene increases the plasticity somewhat at low and high temperatures. p-Nitrosodiphenylamine appears to have little effect on the plasticity, but an examination of the data shows that this batch does not have the normal relation between the softness and the retentivity factors. This departure indicates that some fundamental change occurred in the rubber. This is shown more clearly in Fig. 2, where the softness factor is plotted against the retentivity for these samples.

The smooth curve shows the normal relation for rubber masticated without the addition of any chemical. It is seen that the points for the control batch masticated at high temperatures and at low temperatures fall close to this curve, as do the points for rubber containing nitric acid and azoxybenzene. The rubbers treated with the other chemicals have abnormally low retentivity factors for their softness, just as have reclaims or compounded batches which are scorched. Inasmuch as other stiffeners such as light calcined magnesia do not cause such wide deviations from the normal softness-retentivity relations, it is possible that the effect of the nitroso compounds may be due to some special chemical reaction producing cross-links in the rubber structure. Heating the rubbers which were milled at 165° or 240° F. in a press for 60 minutes at 287° or 350° F. usually increased both the plasticity and the deviations from the normal softness-retentivity relation. The batches masticated at 320° F. were not affected appreciably by these subsequent heat treatments. These reactions appear to be worthy of further study by chemical as well as physical methods.

(2) Effect of Oxygen Concentration on Rate of Breakdown

(a) Rubber.

Smoked sheet was masticated in atmospheres containing different percentages of oxygen to see if this would give any clues to the mechanisms of the high and low temperature reactions. Masticated smoked sheet (initial plasticity 6.5 ± 1.5) was remasticated for 20 minutes at various temperatures while surrounded by atmospheres of commercial nitrogen, air, oxygen and ozonized oxygen, and the final plasticities were measured at 158° F. Since these samples all showed normal softness-retentivity relations, only the plasticity figures are reported here.

Curve A of Fig. 3, for rubber masticated in air, is a composite curve of more than one hundred tests made over a period of several years, the average deviations of the individual readings being shown by the vertical lines through the points. Since these plasticity data were taken at 158° F. the curve is lower than Curve B of Fig. 1, for which the plasticity measurements were made at 212° F., but the curves are of the same general shape.

When the oxygen concentration is reduced by displacing most of the air with nitrogen, the rate of breakdown is very much less, as shown in Curve B. In this test the nitrogen was taken from a tank without any purification and no precautions were taken to remove the last traces of oxygen from the initial rubber, so that the mastication may have been done in an atmosphere containing 0.5% oxygen or more. It will be noted that when the rubber is masticated in this atmosphere at 160° F., the plasticity increases from 6.5 to 10. This increase of 3.5 points is roughly only one-fifth as great as when the mastication is done in air at the same temperature. However, the batches masticated at 240° F. and 320° F. in this low oxygen concentration show no increase, and possibly even some decrease in plasticity.

When the oxygen concentration around the rubber is increased to almost 100% by the use of compressed oxygen, the results shown in Curve C are obtained. It is surprising to find that in the low-temperature range the high oxygen concentration actually lowers the final plasticity of the batch, and so presumably reduces the rate of breakdown compared with the batches masticated in air. At higher temperatures the increased oxygen concentration greatly increases the rate of breakdown.

When the rubber is masticated in an atmosphere of ozonized oxygen, made by passing the oxygen through a commercial ozonizer (inner and outer electrodes

about 4.5 inches and 5.5 inches in diameter, respectively, and 32 inches long) the rate of mastication increases continuously as the temperature is raised from 170° to 330° F., as shown in Curve D.

Plasticity measurements are not a very satisfactory quantitative measure of the extent of the chemical reactions occurring during the high- and low-tempera-

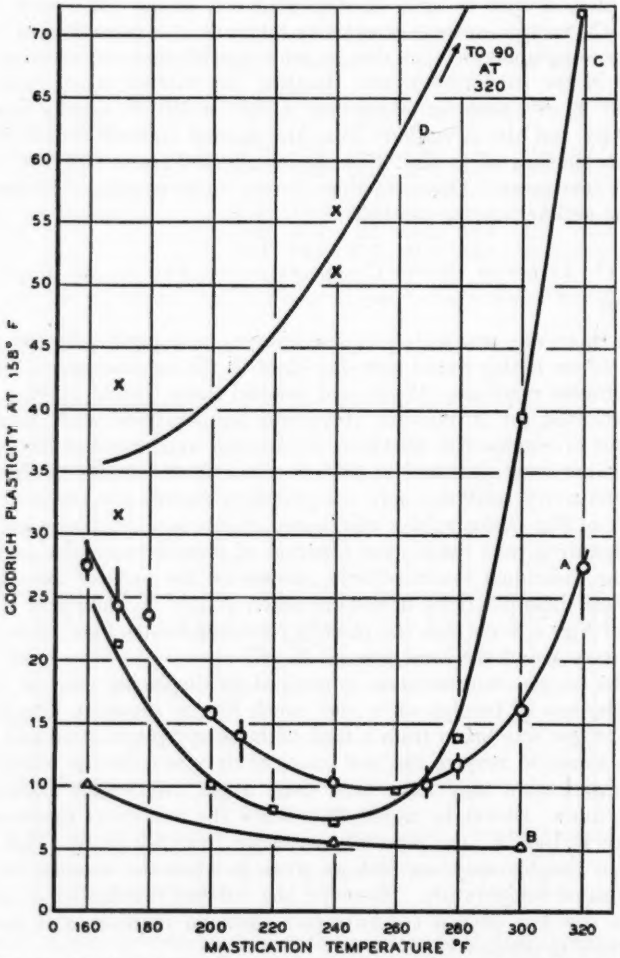

FIG. 3.—Effect of temperature on the rate of breakdown of smoked sheet masticated in various gases.
A—Air; B—Commercial nitrogen; C—Oxygen; D—Ozonized oxygen.

ture mastication of rubber, but in the absence of any better methods they may be used with discretion to furnish some clues about the reactions involved. The plasticity tests show the sensitiveness of the high temperature breakdown of rubber to changes in the oxygen concentration of the atmosphere in the range of 20 to 100% oxygen, which again suggests that this reaction is very similar to

thermal oxidation of the rubber. Since crude rubber heated in air first becomes very soft and tacky, and ultimately hard and brittle on the surface, while rubber a small fraction of an inch under the surface may be affected only very slightly, the rate of reaction of rubber with oxygen at these temperatures is evidently high compared to the rate of diffusion of oxygen through the rubber. This suggests that the mechanical working of rubber in high-temperature mastication speeds the reaction largely by continually renewing the surface of rubber and exposing fresh rubber to the relatively high concentration of oxygen in the surrounding atmosphere.

Ozonizing the oxygen increases the rate of breakdown at temperatures around 270° F., possibly either by furnishing more activated oxygen atoms that can combine with the rubber to produce the same compounds (peroxides?) formed by the normal thermal reaction, or it may break down the rubber molecules by another mechanism involving the formation of ozonides.

The low-temperature breakdown of rubber during mastication must occur through an entirely different mechanism, or at least be limited by different factors. The appreciable breakdown which occurs during mastication in nitrogen at 175° F. may be due either to traces of oxygen which are present or, conceivably, to a purely physical effect such as the breakdown of some mechanical structure. The latter explanation does not seem probable, however, since such mechanical structures should be broken down also by mastication at higher temperatures. The results might be explained by assuming that at low temperatures all the rubber molecules activated by the mechanical distortions quickly react with oxygen to form addition products (primary peroxides), which are fairly stable, but which slowly break down; and that this decomposition reduces the length of the rubber chain and liberates volatile peroxides, which can be detected with a photographic plate. Here the decomposition of the primary addition product is the slow reaction which limits the overall rate. If the number of activated rubber molecules is small, only a relatively low concentration of oxygen at the surface is needed to react with them, so larger concentrations of oxygen do not have any additional effect.

The assumption that the primary addition product is fairly stable is consistent with the fact that volatile peroxides are given off from rubber in quantities sufficient to be detected by a photographic plate for a week or more after the rubber has been cold-masticated[7]. This picture of the mechanism of breakdown is supported also by the fact that smoked sheet or pale crepe rubbers which have been masticated on a very cold mill (below 80° F.) and so presumably contain large amounts of peroxides, are permanently softened by heating about 15 hours at 145° F., or about 3 hours at 212° F. However, it must be noted that in some cases this rapid softening can be produced just as well if the rubber is heated a month after milling as when it is heated a day after milling, so this effect will require much more investigation before it is understood.

The fact that the rate of breakdown is apparently less in pure oxygen than in atmospheric air is very difficult to explain. Oxygen might possibly act in part as a vulcanization agent, as does benzoyl peroxide, or the air might contain some impurity that acts as a mastication catalyst. A number of attempts were made to increase the rate of breakdown in oxygen by adding to the oxygen the vapors of polar materials such as water, acetic acid, acetaldehyde, butyl chloride and methyl alcohol, without very much success. However, it was found that if compressed air from a tank were passed through the mixer instead of merely leaving the hole in the lid of the mixer open to the room air, the rate of break-

down at 180 ° F. was reduced to about that in pure oxygen. This suggests either that room air contains an impurity which acts as a catalyst, or perhaps that the volatile peroxides or other materials formed during mastication act as catalysts, and the rapid flow of the compressed air or oxygen sweeps these catalysts away from the rubber. Again, more information is needed before a satisfactory explanation can be given.

(b) Rubber Containing Softeners.

It was shown above that different softeners may produce their greatest effects in rubber at different mastication temperatures, but the tests did not give much information about the mechanisms by which the softeners acted. Further tests were made by masticating matches containing various softeners in atmospheres having different amounts of oxygen and over a range of temperatures to determine, if possible, whether any of these softeners acted directly on the rubber, or whether they merely accelerated the rate of reaction with oxygen during mastication.

Table IV

Effect of Softeners on Plasticity of Smoked Sheet Masticated in Nitrogen

Material added	Amount (%)	Plasticity at 158° F. when masticated: 20′ at 175° F.	20′ at 240° F.	10′ at 320° F.
None	—	10.0	5.4	5.5
White mineral oil	3.0	11.9	6.6	7.5
Lauric acid	3.0	13.2	8.6	10.6
Zinc laurate (Laurex)	3.0	12.6	5.7	7.0 †
Retort pine tar	3.0	13.6	7.9	8.0 †
Sulfurized terpene	3.0	13.7	8.2	7.0
Butylamine	1.0	14.7	13.8	11.8
Phenate *	0.2	9.9	7.3	9.8
p-Thiocresol	0.2	21.4	8.3	10.7

* Phenate is the zinc acetate double salt of phenylhydrazine.
† These values may be in error by as much as one unit as they were interpolated from the results of the 20 minute mastication.

In these tests the mill-masticated smoked sheet (initial plasticity 6.5 ± 1.0 at 158° F.) was given a 3-minute breakdown, then the chemical was added without opening the mixer and the mastication was continued, usually for a total time of 20 minutes. In some cases also samples were removed at 10 minutes. This required opening the lid, and if the mastication was done in nitrogen, the mixer was then flushed out for 3 to 5 minutes before resuming the mixing. The results of the mastication tests in at atmosphere of nitrogen are shown in Table IV. These data must again be interpreted as showing the effect of mastication in a low concentration of oxygen.

Through an error some of the batches run at 320° were masticated only 10 minutes. Since samples were taken also from most of the batches at the end of 10 minutes, all the data are given for 10-minute mastication at this temperature. Where samples were taken at both 10 and 20 minutes, the difference in plasticity due to the additional mastication usually was only 2 or 3 points. This, of course, would not be true of batches masticated in air or oxygen.

It is seen from these data that the addition of 3% of mineral oil does not change the plasticity of the rubber by more than one or two points. Laurex, pine tar and sulfurized terpene have little, if any, more effect than mineral oil, and even 3% lauric acid has only a slight effect in increasing plasticity when

mastication is done in a low concentration of oxygen. Butylamine appears to have considerable effect on plasticity at all temperatures, which suggests that it may possibly have a direct softening effect on rubber which is not related to the oxidation reactions normally occurring during mastication; however, this was not confirmed in later tests. Both Phenate and *p*-thiocresol cause some softening at 320°, and one of them also at 175°, but the lack of any great effect on rubber at 240° F. shows that their effect cannot be due to a pure peptizing action.

Because of the difficulties of getting all oxygen out of rubber, and the chance for some oxygen to remain in the atmosphere in the mixer, some of the above

TABLE IV (*a*)

EFFECT OF SOFTENERS ON PLASTICITY OF SMOKED SHEET MASTICATED IN NITROGEN

Chemical added	Amount (%)	Plasticity at 158° F. when masticated 15 minutes at: 175° F.	240° F.
None	—	13.9	10.5
Zinc laurate	3.0	12.7	8.4
Phenate	0.5	24.7	13.7
Phenate	0.2	18.1	11.1
Lauric acid	3.0	17.3	9.8
None	—	14.3	7.9
p-Thiocresol	0.5	26.7	11.9
p-Thiocresol	0.2	26.0	13.9
Butylamine	1.0	19.8	7.9
None	—	19.2	11.3

TABLE V

EFFECT OF SOFTENERS ON PLASTICITY OF RUBBER MASTICATED IN AIR

Material added	Amount (%)	Plasticity at 158° F. when masticated at: 175° F.	240° F.	320° F.
None	—	25.7	12.0	26.3
Mineral oil	3.0	—	10.8	31.5
Lauric acid	3.0	29.4	15.5	—
Zinc laurate	3.0	27.2	14.2	34.6
Retort pine tar	3.0	29.8	11.8	19.0
Sulfurized terpene	3.0	21.3	10.6	33.4
Butylamine	1.0	—	24.9	29.1
Phenate	0.2	25.0	19.4	36.4
Phenate	0.5	49.9	42.0	—
p-Thiocresol	0.2	27.5	18.3	53.4

tests at 175° and 240° F. were repeated. The clearance between the blades and shell had been reduced before these tests were run, so the masticating time was reduced to 15 minutes. The results shown in Table IV (*a*) were obtained when starting with smoked sheet having an initial plasticity of 7.1 ± 1.1. The batches were run in the order listed, all the 175° tests being run and then all the 240° tests.

In this series none of the chemicals has much effect at 240° F., so the breakdown obtained at 175° F. is probably due to traces of oxygen.

If the same materials are added to batches masticated in air, the results shown in Table V are obtained. Here all the batches were masticated 20 minutes.

None of these materials has any profound effect on the rate of breakdown at 175° F. except the 0.5% concentration of Phenate. This contains only about

50% of the active ingredient, phenylhydrazine, so about 0.25% of this active ingredient raises the plasticity from 25.7 to 49.9. Since the original rubber had a plasticity of about 6.5, the increase in plasticity was 19.2 for the control and 43.4 for the sample with Phenate. The rate of breakdown was more than doubled.

The data for mastication at 240° F. are the most reliable in the Table, since here the results are less sensitive to slight changes in batch temperature. The increase in plasticity of the control is 5.5 points, while the sample with 0.5% Phenate increases in plasticity by 35.5 points, or nearly seven times as much. The addition of only 0.2% Phenate or of *p*-thiocresol more than doubles the rate of breakdown at this temperature. This is a greater effect than can be obtained from 3% of lauric acid. At 320°, *p*-thiocresol and Phenate are remarkably powerful softeners, having a different order of activity from anything else in the Table. Other data show that the hydrazine compounds may be somewhat less effective than the thiocresols at high temperatures, perhaps because the hydrazine compounds are unstable.

TABLE V (*a*)

EFFECT OF SOFTENERS ON PLASTICITY OF SMOKED SHEET MASTICATED IN AIR

Chemical added	Amount (%)	Plasticity at 158° F. when masticated at: 175° F.	240° F.
None	—	28.4	12.4
Zinc laurate	3.0	26.4	19.5
Phenate	0.5	64.8	72.4
Phenate	0.2	30.0	36.3
Lauric acid	3.0	35.7	15.6
None	—	38.3	9.8
p-Thiocresol	0.5	50.8	50.5
p-Thiocresol	0.2	47.2	41.6
Butylamine	1.0	41.1	13.5
None	—	33.9	10.2

Some of the above softeners were retested to determine their effect on the rate of mastication in air; at the same time the data of Table IV (*a*) for mastication in nitrogen were obtained. The results are shown in Table V (*a*).

The variation in the plasticity of the controls in the tests of Table V (*a*) is somewhat greater than usual, but the data agree with the data of Table V in showing that both Phenate and *p*-thiocresol are much more active softeners than any of the other chemicals. These materials appear to be true "mastication accelerators."

Table VI summarizes the tests showing the effect of adding various softeners to rubber masticated at 240° F. in various gases. The data for mastication in ozone are not very reliable, due to the vagaries of ozone generators, and the result for butylamine in nitrogen could not be checked (see Tables IV and IV (*a*)) but the rest of the data should be fairly reliable.

The data support the view that the mastication accelerators such as Phenate and *p*-thiocresol act by catalyzing the normal high-temperature oxidation reactions during mastication.

SUMMARY

The rate of breakdown of smoked sheet, pale crepe, and sprayed-latex rubber in a laboratory internal mixer is a minimum at temperatures around 240° F., and

the rate may be increased as much as four- or five-fold by either raising or lowering the temperature 80° F.

The high-temperature reaction (above 240° F.) probably is similar to the thermal oxidation which occurs when rubber is heated in air, since the rates of both reactions are increased by increasing the oxygen concentration, and they are reduced by adding antioxidants.

The low-temperature reaction (below 240° F.) may involve a mechanical activation of the rubber, as in milling. The rate of this reaction first increases and

TABLE VI

EFFECT OF SOFTENERS ON PLASTICITY OF SMOKED SHEET MASTICATED AT 240° F. IN VARIOUS GASES

Softener	Amount (%)	Plasticity at 158° F. when masticated in: Nitrogen	Air	Oxygen	Ozonized oxygen
None	—	5.4	11.0–12.0	7.0	23.2–57.1
White mineral oil	3.0	6.6	10.8	8.3	52.7
Lauric acid	3.0	8.6	15.5	11.8	—
Zinc laurate	3.0	5.7	14.2	14.0	74.0
Retort pine tar	3.0	7.9	11.8	9.8	41.8
Sulfurized terpene	3.0	8.2	10.6	10.4	40.3
Butylamine	1.0	13.8	24.9	26.6	65.1
Phenate	0.2	7.3	20.0	43.5	80.7
p-Thiocresol	0.2	8.3	18.3	86.6	89.6

Plasticity of initial rubber: 6.65 ± 1.5.

then remains constant or decreases slightly as the oxygen concentration in the temperature during mastication is increased from about 0.5% to 20% to 100%.

Some nitroso compounds are powerful stiffeners of rubber, and they change the softness-retentivity relation, making it more like that of reclaim or semi-vulcanized rubber.

The effect of most commonly used "softeners" on the plasticity of rubber is small compared with the effect of changing the mastication temperature ±40° F. Exceptions to this are certain vulcanization accelerators (at high temperatures), hydrazine compounds and thiophenols, which appear to be true mastication acelerators or oxidation catalysts.

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TACKINESS AND CONSISTENCY OF RUBBER AFTER TREATMENT BY ALKALI *

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Our knowledge of the chemistry of tackiness in plantation raw rubber is still incomplete. We know that under different circumstances distinct types of tackiness develop. Traces of copper, for instance, cause rubber to liquefy, with formation of a sticky, transparent mass, which then gradually hardens, first on the surface and afterwards throughout, whereby it is transformed into a hard and brittle resin-like substance, easily soluble in acetone. The viscosity of a 1% benzene solution[1] decreases from the normal figure of 30 to, say, 2. This type of tackiness is independent of light, as it develops quite readily in the dark. It is accompanied by an increase in weight[2] of 7 to 13%. The change is regarded as an oxidation catalyzed by copper, but more knowledge about the course of this oxidation and the intermediate and ultimate products would be welcome.

Hydrochloric acid, for instance when used as a coagulant, causes another characteristic form of tackiness, which is very dependent on the action of light, one side of a piece of crepe, for instance, becoming sticky and liquefying, while the other side, turned away from the light, shows no change. During this process also the rubber changes[3] into transparent, yellow oily products, which gradually become hard and brittle; the increase in weight is 9 to 12%.

These types of tacky rubber develop odorous, volatile products (aldehydes?), which cause in wood, and also in crepe rubber[4], a deep violet discoloration somewhat similar to the well-known furfural reaction with a chip of wood.

Still another type of tackiness develops in raw rubber under the influence of alkali, as, for instance, in rubber from latex to which 2% or more of sodium hydroxide has been added. The rubber gradually becomes sticky, in the dark as well as in the light, and runs together into an opaque, formless mass[5]. It does not, however, harden and form resin-like substances, as in the former two cases; only after very prolonged keeping does the surface become hard and glassy.

Several theories have been put forward as to the mechanism of this latter type of decomposition. The influence of alkali on raw rubber gave rise to serious misgivings in the early days, but later it was felt[6] that there was no reason for this, as alkali and alkaline products are so frequently used in compounding without causing any trouble or injury. Alkali added to dry raw rubber proved to be harmless, but rubber from alkaline latex showed a more or less pronounced tendency to tackiness, depending on the chemicals used and their concentration[7]. The opinion was then put forward[8] that alkali removes certain components that have a protecting action; thus, there might be a protecting layer, for instance of proteins, without which the particles are exposed to the oxygen of the air and become tacky by oxidation. For an explanation of this kind it would be necessary to suppose that the rubber hydrocarbon itself is easily oxidizable. This brings us into the interesting subject of the removal of the proteins and its influence on the structure and

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the stability of the rubber particle; a field in which not only the "protective covering" comes into play, but also the "stabilizing layer of protein," which is said to be a factor in the stability of the suspended rubber particles in latex, and the "rigid outer shell," supposed to give a definite, mostly oval but sometimes pear-shaped, form to the rubber particle in latex, the interior of which is regarded as being in the liquid state. It would be of great interest if deproteinized latex could be studied in greater detail in various respects, such as its stability, its coagulation phenomena, and the consistency and durability of the rubber obtained from it. As pointed out on a former occasion[9], a number of observations on fresh latex and rubber are not easily reconcilable with the view that the rubber particle consists of a harder shell and a liquid or jelly-like interior. In our opinion, it is more probable that the rubber particle in fresh latex is solid, though more or less plastic, throughout, and that proteins, lecithins, lipins, resins, and similar substances are partly enclosed in it or dispersed through it (perhaps by reason of its being an organic product), and that these substances are only partly absorbed as a surface layer or precipitated on the particle during coagulation and drying. Further detailed research will be necessary to prove or disprove this view; meanwhile, for our present subject, we have to discuss the hypothesis that removing a

TABLE I

Sample	Diluted with volumes of water	Viscosity after months			
		1	7	11	13
A	1	21	4½	3	2
B	17	21½	8	6	3½
C	33	23	8	6½	8

latex component or a covering layer of proteins causes tackiness by leaving the rubber hydrocarbon bare and so accessible to the oxygen of the air. There are, in our opinion, many facts that point against a marked susceptibility of the hydrocarbon in *Hevea* rubber to oxidation; indeed, most of the facts distinctly indicate that rubber hydrocarbon is in itself comparatively stable and not easily oxidized. In the case of tackiness induced by alkali, several observations led us to the hypothesis[10] that a decomposition product, formed by the action of alkali on some serum component, acts as a catalyst of oxidation and is the cause of tackiness in this case. We have not yet however put forward the facts which prove this supposition; these are set out below.

Removal of the protecting layer of proteins is effected by keeping the latex after adding 2% sodium hydroxide. The greater part of the proteins is thereby dissolved, and if they form a covering surface layer it is necessary to assume that the particle is denuded of this layer. Subsequent coagulation of the rubber after considerably diluting the latex or cream should promote the removal of by-substances. If the theory of a protecting substance or a protecting layer is correct, therefore, rubber obtained from diluted alkaline latex should show an increased tendency to tackiness. To test this point, we diluted the cream from a latex, which had stood for a considerable time with 2% NaOH, with different amounts of water; after stirring and after rubbing down the lumps by gentle pressure, the rubber was coagulated and creped, the air-dried rubber being then kept in a dark cupboard. The figures for viscosity are given in Table I.

Dilution, therefore, diminished the tendency to softening, instead of increasing it. Tackiness had developed in sample A after 7 months; sample B by that time showed only slight traces of it, and sample C none. The same order was maintained as tackiness increased on further keeping.

The crepes were kept in the form of tight rolls; tackiness developed on the outside, but not, or very much more slowly, inside the rolls, showing that for this form of tackiness contact with the air, *i. e.*, oxidation, has to come into play.

A further experiment was made with freshly rolled crepe, which was kept for one hour and for 24 hours respectively in a sufficient quantity of 1% sodium hydroxide solution, a treatment which caused the crepe to become decidedly tacky on keeping. Half of each sample was hung to dry without further treatment, while the other half was well washed with water to remove sodium hydroxide and other soluble products. These samples gave the figures shown in Table II.

The figures for ash give a good idea of the treatment to which the rubber had been subjected; the nitrogen content is hardly affected by this short treatment. The differences among the changes in viscosity on keeping are pronounced. Treatment with 1% NaOH for one hour caused the rubber to soften on keeping; tackiness could be detected by hand after one year and gradually developed further. Washing, however, removed the cause of tackiness, so that the viscosity decreased only slightly more than that of the control sample, while after 1½ years only a slight degree of stickiness had developed. Treatment for 24 hours greatly increased the tendency to tackiness; the viscosity showed a rapid fall, and tackiness was observable after 6 months and strongly developed in a year. Washing restored the keeping qualities to a certain extent.

Table II

Sample	Description	Ash %	Nitrogen %	Viscosity after months 1	7	12	19	24
D	Control	0.24	0.36	38	35	30	29	27
E	NaOH, 1 hour	0.48	0.33	31	25	21	13	13
F	Same, washed	0.37	0.33	40	43	30	24	21
G	NaOH, 24 hours	0.48	0.32	28	6½	4	3½	3
H	Same, washed	0.34	0.32	40	23	15	11	11

These observations show clearly that a water-soluble agent plays a part in the development of this type of tackiness; as sodium hydroxide itself has not this property, a product formed from the by-substances of the rubber must be the causative factor.

Several additional experiments were made, the rubber being treated not only by sodium hydroxide but also by alkaline serum (from the preparation of rubber cream by adding alkali to latex), in which decomposition of serum substances by sodium hydroxide had gone on for a considerable time. The result was always a rubber that became tacky on keeping, often to a very marked degree. To corroborate this statement it is sufficient to mention the results of one experiment, in which freshly prepared crepe was kept for 24 hours in:

Fresh, ordinary acetic acid serum (samples M and N).
Same, made alkaline by NaOH (O, P).
Alkaline serum, old sample (R, S).
Same, made slightly acid (T, V).

Half of each sample was rinsed for a moment in water to remove the adhering liquid (M, O, R, and T); the other half was soaked for 24 hours in a large amount of water to remove soluble substances as far as possible (N, P, S, and V).

The viscosity figures are reproduced in Fig. 1, where K and L are control samples; it will be seen that both alkaline liquids caused a decrease in viscosity, which was accompanied by a gradually developing tackiness. The causative sub-

stance was, however, completely removed by soaking in water. Acetic acid serum and acidified old alkaline serum did not contain the substance that caused tackiness.

In Table III are given the figures for plasticity (thickness of a ball weighing 0.4 g. after pressing for 30 minutes in a plastimeter of the Williams type[11]) for this series of samples; they indicate the same conclusion as the viscosity data in Fig. 1.

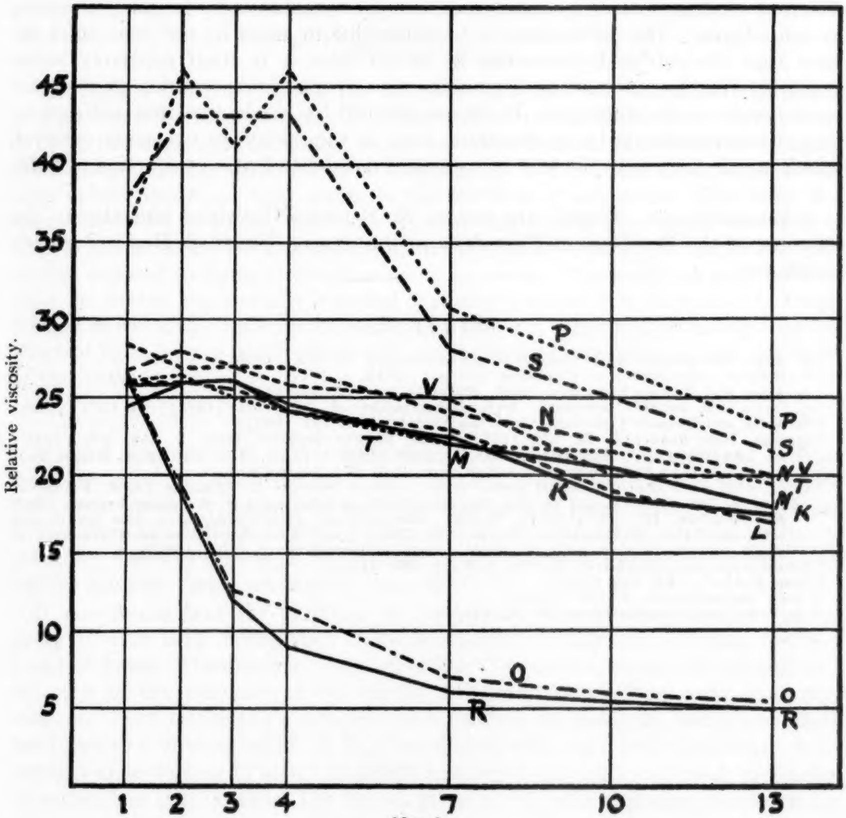

FIG. 1.

TABLE III

Sample	Description	Ash %	Nitrogen %	Plasticity (thickness) after months 1	3	7	13
K	Control	0.28	0.37	1.25	1.15	1.24	1.25
L	Control, soaked 24 hours in water.	0.26	0.37	1.20	1.05	1.06	1.15
M	Acetic acid serum.................	0.25	0.38	1.21	1.14	1.18	1.30
N	Acetic acid serum, soaked........	0.29	0.38	1.17	1.07	1.05	1.18
O	Alkaline fresh serum............	0.51	0.36	1.39	1.05	0.74	0.67
P	Alkaline fresh serum, soaked.....	0.33	0.31	1.29	1.08	1.27	1.23
R	Old alkaline serum.............	0.55	0.35	1.36	0.95	0.52	0.57
S	Old alkaline serum, soaked.......	0.35	0.30	1.27	1.15	1.18	1.25
T	Acidified old alkaline serum......	0.27	0.42	1.33	1.10	1.17	1.29
V	Acidified old alkaline serum, soaked	0.27	0.36	1.19	1.13	1.09	1.23

These investigations seem to indicate clearly that tackiness induced by alkali is caused by a decomposition product of one of the by-substances in latex, formed when a sufficient degree of alkalinity (1% sodium hydroxide or more) is reached, this product being water-soluble and losing its catalytic effect when acidified. The nature of this decomposition product has not yet been elucidated. Several ways suggest themselves for relating it to one of the groups of serum substances or by-products, for instance by preparing serum or rubber containing different combinations of by-substances, *i. e.*, by coagulation by freezing, creaming or centrifuging. The phenomena of tackiness due to alkali do not contradict the view that the rubber hydrocarbon in *Hevea* latex is in itself relatively stable towards oxidation; a coating of proteins or a special latex component does not seem necessary to protect it. Tackiness induced by alkali, like that induced by copper compounds or by hydrochloric acid, is caused by an oxidation catalyst, which in this case, as in the case of copper, is not dependent on the action of light.

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EFFECT OF LIGHT ON UNVULCANIZED RUBBER *

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INTRODUCTION

Although it has been known for centuries that light affects rubber, the action is still among the least understood changes which rubber undergoes. On exposure to light, but under no mechanical strain, vulcanized rubber develops a chalking on the surface and a network of very shallow cracks. If it is under mechanical tension deep cracks appear at right angles to the direction of the stress. This latter is a secondary effect however, since van Rossem[1] has shown that direct exposure to light is not necessary for its production and that ozone is probably the cause. Raw rubber exposed to sunlight becomes sticky or tacky. This tackiness may increase until the rubber is practically liquefied or it may decrease and the rubber be transformed slowly into a resinous material. This paper is concerned primarily with the effect of light on raw rubber and with the catalysis (both positive and negative) of this effect.

EXPERIMENTAL

A series of mixtures of pale crepe with various substances was prepared. Mixing was performed on a standard laboratory mill and the conditions were standardized both as to time and to temperature. Sheets of each of these mixtures were placed 40 cm. from the bulb of a General Electric S-1 lamp, whose radiation is similar to and three times as intense as June sunlight. The temperature of the air surrounding the samples varied between 40° and 44° C.

It was found that the majority of the rubber mixtures investigated became tacky at some time during their exposure, maximum tackiness occurring between 2 and 48 hours. The degree of tackiness after 18 hours' exposure was adopted as a criterion of the intensity of the effect. Arbitrary values from zero to 5 were assigned. Zero represents a sample which exhibits no tackiness, and 5 one which has fused to a viscous liquid. It was found that, with very little experience, independent observers could assign tackiness numbers to samples and check each other to within less than a unit. The figures given in the following data represent the opinion of more than one observer.

In our first experiments 2% of each of several representative antioxygens was used. Blanks of unmilled rubber and rubber milled according to the standard procedure were also subjected to the treatment.

If we are to accept the idea that tackiness is due to the formation of an oxidation product of rubber, the results given in Table I are unexpected, since each of the samples containing an antioxygen is far more tacky than the blank. Furthermore, the effect cannot be attributed to a particular chemical structure of the antioxygen, since the antioxygens tested represent a wide variety of chemical compounds. These materials are excellent preservatives of vulcanized rubber in various accelerated aging tests involving oxidation. Not only do they fail to protect unvul-

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canized rubber from the action of light and oxygen under the conditions of our test, but they are apparently positive catalysts of this deterioration.

We have found also that the tackiness of pale crepe after exposure to the S-1 lamp for 18 hours increases with an increase in the time of milling. It has been reported[2] on the other hand that mastication increases the stability of rubber to light.

The effect of a number of other materials (using 2% of each) on pale crepe was ascertained in the same manner as above, with the following results (Table II) arranged in the order of increasing tackiness.

TABLE I

Material	Antioxygen	Tackiness number. 18 Hours S-1 lamp
Unmilled pale crepe..	—	1
Milled pale crepe....	—	1
" " "	Phenyl-β naphthylamine (AgeRite Powder)	3
" " "	Di-β naphthyl-*p*-phenylenediamine (AgeRite White)	3
" " "	Complex phenolic compound (AgeRite Alba)	2
" " "	Ketoneamine condensation product (BXA)	3
" " "	Polymerized trimethyldihydroquinoline (AgeRite Resin D	4
" " "	*p*-Phenylphenol (Parazone)	4

TABLE II

Material added	Tackiness number. 18 Hours S-1 lamp
Benzidine	0
Sulfur	0
Hydroquinone	0
p-Aminophenol	0
Phenol	1
Resorcinol	1
Catechol	1
p-Phenylenediamine	1
Mercaptobenzothiazole (Captax)	1
Blank	1
Tetramethylthiuram disulfide (Tuads)	2
Zinc butylxanthate (ZBX)	2
Diphenylguanidine (DPG)	2
Copper Inhibitor X872A	3
β-Naphthylmercaptan (R.P.A. No. 2)	3
Manganese stearate	4
Copper stearate	4
Benzoyl peroxide	5

The effects of these materials vary over a wide range. The first four are apparently superior to regular antioxygens in the preservation of unvulcanized crepe. This lends additional evidence to the idea that the deterioration of raw rubber under these conditions is produced by an entirely different process from that which occurs during the aging of vulcanized rubber since benzidine and sulfur are known to have but a slight effect on the aging of the latter. Hydroquinone and *p*-aminophenol[3], however, appear to be preservatives of both vulcanized and unvulcanized rubber. Samples containing these four substances have been exposed with the blank to the action of light and air for much longer periods, and under these conditions their protective action is much more evident.

At present the significance of the other tackiness numbers of Table II is not obvious. It might be noted, however, that the Copper Inhibitor acts similarly to

the antioxygens; that β-naphthylmercaptan, a known plasticizer and therefore perhaps an oxygen carrier, gives a moderately high tackiness number; and that benzoyl peroxide, which may under certain conditions improve the physical properties of rubber by vulcanization, brings about under these conditions a high degree of deterioration.

Since substances have been found which stop the development of tackiness in raw rubber, it seemed possible that they would prevent the positive deteriorating action of other materials. A series of combinations was tested (using 2% of each) with the following results (Table III).

It is evident that in some cases hydroquinone or sulfur is capable of suppressing entirely the action of materials which would otherwise accelerate the deterioration of rubber.

Other experiments with mixtures of two materials, each of which accelerates the development of tackiness, indicate that they produce an additive effect.

TABLE III

Material added	Tackiness number. 18 hours S-1 lamp
Blank (milled pale crepe)	1
Phenyl-β-naphthylamine (AgeRite Powder)	3
Phenyl-β-naphthylamine (AgeRite Powder) + hydroquinone	1
Phenyl-β-naphthylamine (AgeRite Powder) + benzidine	1
Phenyl-β-naphthylamine (AgeRite Powder) + sulfur	0
Manganese stearate	4
Manganese stearate + hydroquinone	1
Copper stearate	4
Copper stearate + hydroquinone	3
Sulfur + *p*-phenylphenol (Parazone)	0
Sulfur + ketoneamine condensation product (BXA)	0
Sulfur + polymerized trimethyldihydroquinoline (AgeRite Resin D)	0
Sulfur + complex phenolic compound (AgeRite Alba)	0
Sulfur + Copper Inhibitor X872A	0

It seemed possible that all the above results might be due to the particular treatment employed. Series of representative samples were therefore exposed to the following agencies:

(1) A mercury vapor quartz arc at 32° C.
(2) Outdoor sunlight at an average temperature of 0° C.
(3) Diffused daylight in the laboratory at an average temperature of 20° C.
(4) S-1 lamp radiation which had passed through 1.25 cm. of glass.
(5) Darkness at 70° C.
(6) Ozone at 20° C.
(7) S-1 lamp radiation through clear fused quartz at a vacuum of 0.01 mm. mercury.

Tests 1, 2, and 3 produced relatively low tackiness, whereas tests 4 and 5 produced tackiness quite similar to the regular S-1 lamp treatment. No tackiness was produced in tests 6 and 7 during 48 hours' exposure.

These tests showed that the relative effects of the various substances were unchanged, but that the time needed to produce a given tackiness figure differed from test to test.

It would appear that the tackiness of raw rubber is produced only in the presence of air and is accelerated by visible light and heat. Ultraviolet light is not essential.

The effect of varying amounts of phenyl-β-naphthylamine was determined. Samples of crepe containing 1, 2, and 4% were exposed to the S-1 lamp. The tackiness developed was in proportion to the amount of antioxygen present.

It was thought that the color of the rubber might have some effect on its sensitivity to this deterioration. Samples of pale crepe were mixed with a sufficient amount of red, yellow, green, or black pigment respectively to give a strong coloration. On exposure to light, development of tackiness seemed to be uniform enough to conclude that color was without effect.

It was thought that some of the substances that activate or retard the development of tackiness by light might have a parallel effect in the plasticization of rubber, since the latter is an oxidation process. Two per cent of each reagent was added to pale crepe and the mixtures were milled on a laboratory mill under standard conditions for a fixed period of time. Williams plasticities were determined at 100° C. The smaller the number the more plastic is the rubber.

TABLE IV

Material	Plasticity
Hydroquinone	2.70
Phenyl-β-naphthylamine	2.74
Blank	2.88
Polymerized trimethyldihydroquinoline	3.08
Benzidine	3.59
p-Aminophenol	3.59

There seems to be no entirely satisfactory correlation between the production of tackiness by the various reagents and their effect on plasticity. Busse[4] found that antioxygens do not retard plasticization.

Considerable attention has been paid in the past to the effect of the naturally occurring acetone-soluble substances on the oxidation of rubber. It is universally conceded that the removal of these from rubber renders the latter far more susceptible to oxidation. This has been ascribed of course to the presence of naturally occurring actetone-soluble antioxygens[5, 6] and these have been partially identified[7, 8]. Various rubbers were extracted with acetone and were exposed to the S-1 lamp radiation. They became much more tacky than the unextracted samples of rubber, showing that the acetone-soluble materials in raw rubber protect it against deterioration by light as well as other oxidations.

A sample of mixed unvulcanized rubber compound containing zinc oxide, an accelerator (benzothiazyl disulfide), an antioxygen (phenyl-β-naphthylamine), and sulfur was exposed to the action of the S-1 light for 18 hours. No tackiness was produced. Even increasing the exposure several-fold produced no apparent change. The subject was investigated further by exposing several mixtures to the light, with the following results:

TABLE V

Material	Tackiness number. 18 hours S-1 lamp
Crepe	1
Crepe + antioxygen	3
Crepe + antioxygen + zinc oxide	3
Crepe + antioxygen + sulfur	0
Crepe + antioxygen + accelerator	3
Crepe + sulfur	0

Sulfur is apparently the component that protects the mixture from becoming tacky.

Although our results are essentially qualitative, we have obtained preliminary measurements on the absorption of oxygen during the exposure of unvulcanized rubber to light. A sample containing 2% phenyl-β-naphthylamine absorbed oxygen at a greater rate than one containing no antioxygen. Further work will be reported later.

The experience of previous authors with the Russell effect would indicate that it accompanies many types of oxidation. Van Rossem[9] has shown that, although ultraviolet light produces the effect readily in raw rubber, this type of illumination

TABLE VI

Rubber	Material	Tackiness number	Russell effect number
Crepe	—	1	2
Crepe (milled)	—	1	2
Crepe (acetone-extracted)	—	4 +	0
Smoked sheet (milled)	—	1 +	5
Smoked sheet (acetone-extracted)	—	4	1
Para	—	1	1
Evaporated latex	—	0	0
Crepe	Phenyl-β-naphthylamine (AgeRite Powder)	3	3
"	Polymerized trimethyldihydroquinoline (AgeRite Resin D)	4	3
"	p-Phenylphenol (Parazone)	4	0 +
"	Benzoyl peroxide	5	5
"	Manganese stearate	4	5
"	Lead dioxide	2	1
"	β-Naphthylmercaptan (R.P.A. No. 2)	3	1
"	p-Aminophenol	0	1
"	Hydroquinone	0	2 −
"	p-Phenylenediamine	1	1
"	Tetramethylthiuram disulfide (Tuads)	2	0
"	Diphenylguanidine	2 +	0
"	Zinc dimethyldithiocarbamate	2	0
"	Mercaptobenzothiazole (Captax)	1	0
"	Sulfur	0	0
"	AgeRite Resin D + sulfur	0	0
"	Parazone + sulfur	0	0
Para	Phenyl-β-naphthylamine (AgeRite Powder)	2	2
Evaporated latex	Phenyl-β-naphthylamine (AgeRite Powder)	2	2

is not necessary, since he obtained a satisfactory Russell effect in diffused daylight. It seemed possible therefore that our results might be related to the Russell effect. A series of representative samples was exposed to the action of the S-1 lamp for 3 hours. The radiated materials were then placed in contact with Eastman No. 50 plates and allowed to remain in the dark. An exposure of the plates to the action of the rubber for 18 hours gave a fairly satisfactory image, but more satisfactory results were obtained with longer exposures (up to 72 hours). The amount of the Russell effect was determined according to an arbitrary scale, in which zero represented no effect and 5 an intense one. As in the case of determining the tackiness of rubber samples according to an arbitrary standard, it was found that with very little experience independent observers checked each other closely.

From the results given in Table VI it may be concluded that tackiness is not necessarily associated with the Russell effect, although the figures are proportional in many cases.

It has been reported also by van Rossem that the Russell effect is reduced to nearly zero by acetone extraction. This agrees with our results. Since this is so, it is possible that the reagents are merely increasing or decreasing the Russell effect of the acetone-soluble substances or have their own effect and are not altering the Russell effect of the rubber hydrocarbon.

It is interesting that, although the vulcanization accelerators used promote the development of tackiness of rubber in light, they eliminate the Russell effect.

Since sulfur seems to suppress completely the development of tackiness and gives no Russell effect, 2% was added to mixtures which gave a strong Russell effect. The Russell effect was suppressed almost completely in every case.

In the light of our experiments, it is interesting to examine van Rossem's results on the Russell effect from compounded rubber. He observed that a mixed rubber compound gave only a very weak Russell effect, which he believed to be due to one of the ingredients acting as a suppressor. The presence of either zinc oxide or diphenylguanidine was found not to interfere with the development of the Russell effect. Although a mixture of rubber and sulfur gave only a very weak effect, he concluded that it was only the combination of all the ingredients which seriously weakened the Russell effect. He concluded further that a combination of the sulfur and diphenylguanidine was most active. He suggested that the two chemicals interact to form a chemical compound which decomposes peroxides. His other results are somewhat at variance with ours, since, of the accelerators that he tested, only mercaptobenzothiazole suppressed completely the Russell effect. He concluded from this that sulfur and diphenylguanidine might be reacting under the influence of light to form mercaptobenzothiazole, which suppressed the development of peroxides. He tested this hypothesis by exposing a benzene solution of sulfur and diphenylguanidine in a quartz container to sunlight for a month, but failed to obtain any detectable traces of mercaptobenzothiazole. He was therefore at a loss to explain why a mixture of sulfur and diphenylguanidine should suppress the Russell effect. By knowing that sulfur is such an active ingredient in this direction, it becomes very easy to explain his results on this basis alone.

Van Rossem has demonstrated that vulcanized rubber compounds give only a very weak Russell effect. Since the Russell effect is neither greater nor less than that for the unvulcanized compound, it is quite possible that this may be ascribed to the presence of sulfur.

DISCUSSION

Gorter[10] showed that tackiness in raw rubber occurs only in the presence of oxygen. Garner[11] found that the development of tackiness and oxidation are concurrent, and believed that these changes are accompanied by either polymerization or depolymerization. He examined also the effect of light on rubber solutions and showed that the viscosity is reduced sharply in the presence of oxygen. He demonstrated also that certain unnamed antioxygens affect the change differently and concluded that the relative action of the various antioxygens was not parallel to their relative effects in vulcanized rubber compounds. Fickendey[12] found that tannin decreases the tendency of raw rubber to become tacky in light.

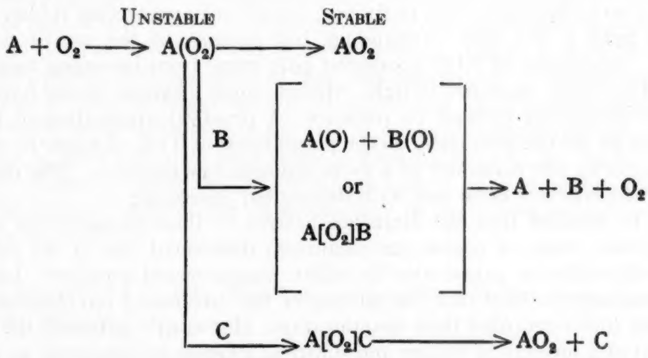
Under certain conditions light renders a portion of raw rubber insoluble in organic solvents[13, 14]. The stickiness developed by unvulcanized rubber on exposure to light is undoubtedly a result of oxidation. The quantity of acetone-soluble material in the rubber increases with time of exposure, but this is complicated by a loss of volatile peroxides. Dekker and van Rossem have described[15] what they believe to be a more sensitive index of the oxidation of rubber in the

presence of sunlight. This involves treatment of the alcoholic potash extract residue with more potash, which removes fat acids from the unsaponifiable oxidation product. This latter material increases rapidly when rubber is exposed to light in the presence of air. The Russell effect suggests also that the action of light on rubber involves oxidation. This is due probably to the presence of volatile peroxides (possibly hydrogen peroxide) formed by the action of light. It is also possible to detect peroxides or at least substances with a strong oxidizing action by chemical means[16, 17, 18].

It has been known for a long time that the oxidation of rubber is sensitive to catalysis of the positive type. Moureu and Dufraisse showed in a series of publications beginning in 1921 that many oxidations can be retarded by negative catalysis and that this control is applicable to rubber. Since that time a host of organic compounds has been proposed for use in rubber to retard its deterioration by oxidation. Their use is almost universal in high-grade vulcanized rubber products today, and they have been instrumental in increasing greatly the life expectancy of rubber compounds.

One of the surprising features of our work is that the materials known as antioxygens are among the most effective reagents in accelerating the development of tackiness of unvulcanized rubber in the presence of light. This would seem to necessitate a reconsideration, at least, of some of the theories on the oxidation of rubber and its control.

The classical theory on the control of the oxidation of rubber by means of antioxygens is that proposed by Moureu and Dufraisse[19]. It may be expressed briefly by the following diagram.



The normal course of oxidation results in the formation of an unstable peroxide of the substance being oxidized (A), which is in turn transformed into a stable oxide. If a negative catalyst such as an antioxygen (B) is present, chemical combination with the unstable oxide takes place, and the product decomposes into the original substances, A, B and free oxygen. If on the other hand, a positive catlyst (C) is present, it combines with the unstable oxide, which is converted to the stable oxide, with regeneration of the positive catalyst.

Bailey[20] has assumed on the other hand that oxidation occurs at interfaces and that the reaction is controlled by preferential adsorption. There is also some evidence of a correlation between the effectiveness of an antioxygen in rubber and its oxidation potential. There is a similar correlation for antioxygens in petroleum products[21], but the absolute correlation values are not the same. A number of

theories of the action of antioxygens involve energy relationships[22, 23], but investigation of these is difficult. It has been suggested[24, 25, 26] that depolymerization accompanies oxidation of rubber. In cases in which peroxides are involved, it might be pointed out that peroxides are frequently catalysts of polymerization[27] rather than of depolymerization.

The effectiveness of commercial antioxygens in the prevention or retardation of oxidation of vulcanized rubber is unquestioned, and Dufraisse[14] and Memmler[28] state that they stabilize raw rubber. Most of the experimental work on antioxygens has utilized artificial aging tests as criteria. These artificial aging tests, involving oxygen, elevated temperatures and darkness, seem to correlate very well with the deterioration of vulcanized rubber in the dark at lower temperatures.

It is somewhat doubtful whether the oxidation of rubber in the dark or at elevated temperatures is accompanied by the formation of peroxides, although it is supposed to be autocatalytic[29].

Our results do not seem to be consistent with the Moureu and Dufraisse theory of antioxygen action. Antioxygens are supposed to decompose any peroxides formed by the action of oxygen and thus retard their harmful effect on rubber. The development of tackiness in unvulcanized rubber by light is accompanied by peroxide formation, but the antioxygens instead of preserving the rubber appear to be positive catalysts for this deterioration.

On the other hand, some materials have a protective action under these conditions; of these, sulfur, hydroquinone and benzidine appear to be the most effective. Even a small percentage of sulfur will stop entirely the vigorous deteriorating effect of benzoyl peroxide.

The protective action of sulfur is interesting, since it has been reported[30, 31] that it has no antioxygen effect in rubber. Its effect in protecting rubber from the action of light is not only outstanding, but extends to the use of very small amounts. Admixture of 0.1% prevented pale crepe from becoming tacky during 5 days' (120 hours) exposure to light, whereas some tackiness would have become evident in two hours without its presence. A practical application of this principle might be the incorporation, on the plantations, of 0.1% of sulfur in all rubber, thereby assuring the consumer of a more uniform raw material. This quantity of sulfur should interfere in no way with subsequent processing.

It will be recalled that the Brazilian natives in their manufacture of rubber articles (which were, of course, unvulcanized) discovered that if the rubber was treated with sulfur or gunpowder its utility was increased greatly[32]. Lüdersdorff advised similarly in 1832 that the dusting of the surfaces of unvulcanized rubber goods with sulfur retarded their deterioration. Hayward[33] patented the exposure to sunlight of a mixture of rubber and sulfur as a means of producing an improved product. This preservative effect has been regarded by some writers as a possible discovery of vulcanization with sulfur.

It is probable that sulfur did combine with the rubber under these conditions, since a sample of crepe containing 2% sulfur gave, on analysis, 0.2% of combined sulfur after exposure to the S-1 lamp for 75 hours. It is possible, however, that combination of sulfur is either incidental or that extremely small amounts are effective, since its preservative action is apparent after one-twentieth of the above time and when only one-twentieth the above amount is present.

It may be pointed out that sulfur acts as an antioxygen for several other substances. Moureu and Dufraisse report[34] for example that 0.01% of sulfur is a very effective antioxygen for benzaldehyde. It also prevents the oxyluminescence of phosphorus, and it retards the polymerization of styrene[35], a reaction catalyzed by oxygen.

Dufraisse has recommended ardently that the products generally called *antioxidants* should be designated as *antioxygens* on the basis that the materials protect against oxidation by gaseous oxygen, but not necessarily against oxidation by other oxidizing agents. Since there is little evidence that peroxides are involved in the rubber oxidations in which these substances are effective and it is possible that these deteriorations involve only the direct action of oxygen, his designation may be the correct one, and we have used it in this paper.

Since sulfur, hydroquinone and benzidine protect rubber from tackiness (which is presumably an oxidation in which peroxides are involved) these substances might properly be called *antioxidants*.

Bierer and Davis[36] demonstrated that oxygen bomb artificial aging tests correlated excellently with natural aging in the dark. On the other hand, they found the correlation did not extend to the natural aging of vulcanized rubber exposed to light. This does not disagree with our present results, although it has been claimed that sunlight is an accelerator of oxidation without altering its nature[37]. Since most rubber goods are used in light, one should be somewhat cautious, perhaps, in predicting their life under such conditions from the results of conventional accelerated aging tests, although Winkelmann[38] has demonstrated that antioxygens do protect vulcanized rubber in sunlight.

The mastication of unvulcanized rubber depends on oxidation, with accompanying formation of peroxides. It is well known that relatively small amounts of benzidine and *p*-aminophenol stiffen masticated rubber. It might be inferred that these compounds are effective in decomposing peroxides of rubber, since they are relatively ineffective as antioxygens in vulcanized rubber. This idea is consistent with the fact that they are apparently preservatives of unvulcanized rubber in the presence of light where peroxide oxidation is involved. Also, since antioxygens are supposed to destroy peroxides and thereby preserve rubber, it might be thought that in the present work the amount used was insufficient to destroy all the peroxides. In that event a larger amount of antioxygen should cause less tackiness, yet the reverse seems to be true in the case of phenyl-β-naphthylamine.

We seem to have but little knowledge of what happens to the rubber molecule when it is exposed to light and air. We wish also to offer no theory of the phenomena but merely point out that a satisfactory theory should include an explanation of the above facts.

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THE DISTRIBUTION OF COMBINED SULFUR IN VULCANIZED RUBBER AND ITS BEARING ON THE SULFIDE LINKAGE THEORY OF VULCANIZATION *

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INTRODUCTION

The early work by Henriques[1] and by Weber[2] on the addition of sulfur chloride to rubber and the work by Weber[3] on the addition of sulfur to rubber served as the beginning of an intensive chemical study of vulcanization. It was more or less natural to assume that the sulfur chloride or sulfur produced the vulcanized condition by uniting the molecules through the double bonds. This view has so dominated the investigation of vulcanization that most of the theories of acceleration do nothing more than propose methods by which the accelerator is able to supply sulfur sufficiently active to combine readily with rubber.

The possibility of producing vulcanization by the simple procedure of linking molecules of rubber together has been a subject for speculation without direct experimental evidence. It is possible that an elastic mass would result from such a process, but it is equally possible that a rigid resinous system would result. Meyer and Hohenemser[4] have shown by the formation of sulfonium compounds that a considerable portion of the combined sulfur is present in the form of thioether. While this shows the linking of two carbons through sulfur, it does not show that the carbons are in different rubber molecules. The change of the α-polymer of chloroprene into β-polymer was stated by Carothers, Williams, Collins and Kirby[5] to be due to cross-linking into a three-dimensional structure, and the explanation has been generally accepted. There is, however, no experimental evidence for the occurrence of such a reaction other than the change in physical properties, and the mechanism which implies the utilization of primary forces is probably incorrect.

One of the most disturbing factors pertaining to the cross-linking theory of vulcanization is the entire lack of relationship between the amount of combined sulfur and the resulting physical properties. Shepard and Krall[6] and Hardman and White[7] have presented data to substantiate this point. Bruni and Romani[8] have shown that the small amount of sulfur available from thiuram disulfide accelerators is sufficient to produce good physical vulcanization. In view of these facts, it is necessary to assume either that sulfur combines to form the thioether linkage in more than one way and that a variable part of the sulfur links the rubber molecules together under different conditions of vulcanization, or that sulfur is distributed differently among the rubber units.

If the mechanical properties of rubber develop because the units are linked together with sulfur, the best physical properties should result when the combined sulfur is uniformly distributed. A nonuniform distribution of combined sulfur would indicate that portions of the rubber are linked together more than

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the average amount with a resulting deficiency in other parts. Such rubber should be weaker than rubber in which all portions are of average strength.

Attempts have been made to show that rubber is not homogeneous in regard to the distribution of combined sulfur. The work of Stevens[9] and of Bacon[10] indicates that rubber is homogeneous in regard to sulfur content. Midgley, Henne, Shepard and Renoll[11] worked with rubber containing 0.06% of combined sulfur, and succeeded in separating fractions of different sulfur content. While this work indicates a nonuniform distribution of sulfur, the amount of combined sulfur was insufficient to produce vulcanization. Because of lack of information on this point, the problem of determining the distribution of sulfur in well vulcanized rubber was undertaken.

EXPERIMENTAL

It is possible under proper conditions to peptize well vulcanized rubber sufficiently to be fractionated. It was shown by Williams[12] that accelerators act as

TABLE I

RUBBER COMPOUNDS

Material	Compound number 1	2	3	4	5
Smoked sheet	100	100	100	100	100
Sulfur	10	10	3	3	—
Zinc oxide	—	—	2	2	2
Butyraldehydebutylamine	—	—	0.5	—	—
Di-*o*-tolylguanidine	—	—	—	1.0	—
Tetramethylthiuram disulfide	—	—	—	—	3
Minutes vulcanization	60	120	30	30	20
Temperature, °C.	148	148	142	142	142

TABLE II

PHYSICAL PROPERTIES OF RUBBER COMPOUNDS

Compound	Modulus, lbs. per sq. in., at an elongation of 400%	600%	700%	Tensile strength, lbs. per sq. inch	% Elongation at break
1	—	125	175	1350	1020
2	—	225	375	1800	980
3	375	1725	4000	4000	700
4	400	1900	3600	4000	730
5	225	900	1875	3300	780

peptizing agents for vulcanized rubber. Rubber vulcanized with sulfur alone or in the presence of the usual medium-strength accelerators is easily brought into solution in aromatic solvents containing piperidine at temperatures below 100° C. Piperidine was used as the peptizing agent in the following experiments because it was found that piperidine and thioethers such as ethyl sulfide will not react when heated together under the conditions used in the peptizing experiments. It was selected also because it contained no sulfur which could become a complicating factor in the analyses. While the peptized solutions are sufficiently fluid to be filtered through paper, they are not highly degraded, and very firm rubber may be recovered by careful precipitation with alcohol.

The properties of the various fractions and the distribution of sulfur were determined in five compounds which were selected to represent various conditions of vulcanization. The composition and vulcanizing conditions of these stocks are shown in Table I and the physical properties are given in Table II.

Peptizing.—The rubber samples, after being vulcanized, were crumbed on a rubber mill and acetone-extracted for five days. The extracted and vacuum-dried rubber was peptized at 95° to 97° C. with 20 cc. of a 5% solution of piperidine in toluene for each gram of rubber. Compounds Nos. 1 and 2 were well peptized in 24 hours. Compounds Nos. 3 and 4 required from 48 to 60 hours to become homogeneous. Compound No. 5 could not be peptized with piperidine at this temperature in 10 days. After heating in a 5% solution of piperidine in *o*-dichlorobenzene for 72 hours at 140° to 160° C., the rubber was in solution, but was in such a softened condition that the fractionation was not completed. The vulcanized rubber sols after becoming homogeneous were filtered through filter paper under suction in order to remove all suspended foreign material.

A peptizing agent is necessary for the production of a homogeneous sol, but the process does not require oxygen. Compound No. 2 swelled but retained its shape after 48 hours in pure toluene at 97° C. The same compound contained in a tube with a 5% solution of piperidine in toluene was boiled under reduced pressure to expel the air and was sealed in this condition. The rubber peptized in the normal manner at 97° C.

Fractionation.—Fractionation of the filtered solutions was carried out in the following general manner. The solution was warmed to about 35° C. in a separatory funnel. A stirrer was introduced into the liquid and warm ethyl alcohol was run in very slowly and with rapid agitation. The addition of alcohol was discontinued from time to time and a test portion removed from the separatory funnel. This portion was cooled slowly and the temperature of precipitation as indicated by sudden clouding was noted. In most cases the temperature or precipitation was adjusted to 32° C.±0.1° C. When the precipitation point was practically reached, the final adjustment for obtaining the first few fractions was of such accuracy that the addition of 0.5 cc. of alcohol to the total volume of 1,500 cc. of solution produced a definite end-point. The contents of the funnel were warmed, if necessary, to 35° C. in order to ensure solution of all of the rubber, and the funnel placed in an oven maintained at 28° C. for 18 hours, while the fraction precipitated. The separation appeared to be due to syneresis of the more vulcanized portion of the rubber, which separated sharply as a viscous layer in the lower portion of the funnel and was withdrawn.

Unaccelerated compound 2 and accelerated compound 3 were separated into nine fractions according to the following procedure.

Method of Fractionation of Vulcanized Rubber

$$
\begin{tikzcd}
A \arrow[r] \arrow[d] & \underline{C} \\
B \arrow[r] & D \arrow[r] \arrow[d] & E \arrow[r] \arrow[d] & P \arrow[r] \arrow[d] & R \arrow[r] \arrow[d] & T \arrow[r] \arrow[d] & \underline{V} \\
G & F \arrow[l] \arrow[d] & \underline{O} & \underline{Q} & \underline{S} & \underline{U} \\
& H \arrow[r] \arrow[d] & J \arrow[r] \arrow[d] & L \arrow[r] \arrow[d] & N \\
& \underline{I} & \underline{K} & \underline{M}
\end{tikzcd}
$$

Arrows point horizontally to homogeneous liquids and upper layers.
Arrows point downward to lower layers or coagula. Fractions are underlined.

A—Treat 50 grams of thoroughly acetone-extracted rubber with peptizing agent in toluene at 95° to 98° C. Filter through paper and coagulate with two volumes of alcohol.
B—Is the resulting coagulum. Dissolve in benzene and coagulate six times with alcohol to remove any remaining peptizing agent. Add all wash liquor to C.
C—Is the liquor from the coagulation of A combined with fractions G and N and all wash liquors.
D—Dissolve the final coagulum from B in 1,000 cc. of benzene and adjust the precipitation point to 32° C. Let stand overnight at 28° C. and separate.
F—Lower layer from D. Make up to 1,000 cc. with benzene and adjust precipitation point at 32° C. Separate at 28° C.
G—Top layer from F. Add to C.
H—Lower layer from F. Make up to 1,000 cc. with benzene and adjust the precipitation point to 29° C. with alcohol. Separate after standing overnight at 28° C.
I —Lower layer from H is the most insoluble fraction. Coagulate with alcohol and mill dry on a hot mill.
J —Upper layer from H. Adjust precipitation point to 30° C. and separate at 28° C.
K—Lower layer from J is the second fraction. Coagulate and mill dry.
L—Upper layer from J. Adjust precipitation point to 32° C. and separate at 28° C.
M—Lower layer from L. Coagulate and mill dry.
N—Upper layer from L. Add to C.
E—Upper layer from D. Adjust precipitation point to 32° C. and separate at 28° C.
O—Lower layer from E. Coagulate and mill dry.
P—Upper layer from E. Adjust precipitation point to 32° C. and separate at 28° C.
Q—Lower layer from P. Coagulate and mill dry.
R—Upper layer from P. Adjust precipitation point to 34° C. and separate at 28° C.
S—Lower layer from R. Coagulate and vacuum-dry at 80° C.
T—Upper layer from R. Adjust precipitation point to about 40° C. and separate at 28° C.
U—Lower layer from T. Coagulate and vacuum-dry at 80° C.
V—Upper layer from T. Evaporate and vacuum-dry at 80° C.

The results of the fractionation of the unaccelerated compound are shown in Table III. It should be noticed that the first fractions, which are also the least soluble, tend to have the smallest amount of sulfur and contain most of the nitrogen. The nitrogen appears to be from the protein which is carried down and makes the first fractions opaque. Only fraction C contains a measurable amount of nitrogen from the peptizing agent. As successive fractions are obtained, the sulfur increases slightly, the nitrogen almost disappears and the fractions become perfectly transparent. The total amount of sulfur and nitrogen in the original rubber is well accounted for. The peptizing process has caused neither a loss of sulfur nor an increase in nitrogen, one or both of which would have been expected if the process involved the rupture of a valence bond.

It was noticed that the original coagulum and most of the fractions were very difficult to dissolve if too much solvent was removed by the alcohol treatment. Fractions can be kept in homogeneous solution and diluted if too much solvent has

not been removed, even after the peptizing agent has been washed out. If sufficient solvent is removed to permit the rubber units to come close together, the product will be extremely difficult to dilute and the removal of more solvent will produce an insoluble coagulum.

TABLE III

FRACTIONATION OF UNACCELERATED VULCANIZED RUBBER COMPOUND No. 2

Fraction	Grams	% S	Grams S	% N	Grams N	Character of rubber
Original	50	4.32	2.16	0.32	0.160	Well vulcanized.
I	3.4	3.57	0.124	2.13	0.073	Opaque, dark grey, insoluble. Mills to a crepe.
K	2.0	3.89	0.078	1.71	0.034	Opaque, insoluble. Mills to a crepe.
M	2.2	3.86	0.085	0.95	0.028	Somewhat opaque, insoluble. Mills to a rough sheet.
O	4.8	3.86	0.185	0.13	0.006	Light amber, transparent, insoluble. Mills to rough sheet.
Q	3.9	3.92	0.153	0.05	0.002	Mills to a rough amber crepe. Dissolves with great difficulty.
S	2.8	4.03	0.113	0.02	0.000	Transparent amber color. Tacky but firm rough sheet on mill. Not readily soluble.
U	4.7	4.06	0.191	0.04	0.002	Dark amber, transparent. Tacky and elastic.
V	7.3	4.37	0.319	0.10	0.007	Brown, transparent, quite soft, elastic mass.
C	17.6	4.67	0.821	contains piperidine.		Dark, very soft, sticky, elastic.
Total of fractions	48.7	—	2.069	—	0.152	

TABLE IV

FRACTIONATION OF RUBBER ACCELERATED WITH BUTYRALDEHYDEBUTYLAMINE

(Compound No. 3)

Fraction	Grams	% S	Grams S	Plasticity	Recovery	Character of rubber
Original	50.	2.41	1.205	Elastic	—	Well vulcanized.
I	2.65	3.91	0.104	Elastic	—	Opaque and insoluble.
K	6.85	3.77	0.258	64	Complete	Opaque and insoluble.
M	4.27	2.65	0.113	37	600	Transparent crepe, insoluble.
O	5.6	1.65	0.093	23	300	Transparent amber crepe, insoluble.
Q	4.7	1.67	0.079	19	450	Clear amber, tacky but firm, difficultly soluble.
S	5.6	1.63	0.091	8	40	Clear amber.
U	0.0	0.00	0.000	—	—	—
V	2.5	1.84	0.046	5	10	Clear, dark amber.
C	16.8	2.04	0.344	—	—	Dark, soft and sticky.
Total of fractions	48.97	—	1.128	—	—	—

The results of the frationation of the compound accelerated with butyraldehydebutylamine are shown in Table IV. In this case the plasticity and recovery of the various fractions were measured with the pendulum plastometer[18]. The first fraction is too elastic for these measurements to be made, and the elasticity of the

following fractions is indicated by the high recovery after deformation. In this case, however, the most insoluble fractions contain the most sulfur. The combined sulfur decreases in the successive fractions until the last two fractions are reached, when a small increase is shown. The distribution of sulfur is far from uniform. If the properties characteristic of a vulcanizate are caused by sulfur bonds, this compound would be expected to be much inferior to compound No. 2, which has more sulfur and a much more uniform distribution of sulfur. The compound containing the smaller amount of sulfur unevenly distributed is, however, much superior in physical properties.

The nitrogen in the various fractions from the accelerated stock was largely confined to the first two fractions, which contained the protein of the rubber. This protein also contains sulfur, but the amount does not seem to be sufficient to alter the results materially. Fraction I was decomposed by heating for 7 hours in menthane at 169° C. Most of the solvent was then distilled off and replaced with ether, after which the solution was centrifuged. The centrifuged liquor was evaporated to give a brown but transparent soft product. The sediment was washed with ether and dried. The amount collected was only about 3% of the weight of the fraction. This is much less than the protein originally contained in the rubber,

TABLE V

PHYSICAL PROPERTIES OF FILM FROM PEPTIZED RUBBER

Modulus, lbs. per sq. in., at elongation of			Tensile strength, lbs. per sq. in.	% Elongation at break
200%	400%	600%		
130	290	580	680	640

part of which was probably removed by filtration of the peptized solution. The sulfur content of the protein was found to be 3.64%; no zinc was present.

The first few fractions of compound No. 3 after evaporation of the solvent are quite insoluble and vulcanized in character. About one-half of I, K, M, and O was mixed and evaporated to form a film which could be tested. The film was insoluble, not tacky and had considerable strength, as indicated by the data in Table V. The ability of these fractions to form an insoluble vulcanized film simply by evaporation of the solvent shows it to be unnecessary to join the units by means of a sulfur linkage to produce the properties of vulcanized rubber.

Although the method of fractionation just described serves to show the extent to which rubber may be separated, the operation is rather extended and a simplified procedure was developed which will adequately distinguish differences in the distribution of sulfur. The separation which follows can be completed in about four days after the rubber is peptized.

SHORT METHOD OF FRACTIONATION

$$
\begin{tikzcd}
 & A \arrow[r] \arrow[d] & G \arrow[r] \arrow[d] & \underline{\ } \\
\underline{F} & B \arrow[l] \arrow[d] & \underline{H} & \\
\underline{E} & C \arrow[l] \arrow[d] & & \\
 & \underline{D} & &
\end{tikzcd}
$$

Arrows point horizontally to homogeneous liquids and upper layers.

Arrows point downward to lower layers or coagula.

Fractions are underlined.

A—Rubber peptized in toluene and filtered through paper. Coagulate with 2 volumes of alcohol. Let stand overnight and decant off the liquid.
B—Coagulum from A. Dissolve in benzene and precipitate with alcohol six times. Add liquor to G. Make coagulum up to 1,000 cc. with benzene. Adjust precipitation point to 30° C. with alcohol and let stand overnight at 28° C.
F—Upper layer from B. Evaporate on steam bath and vacuum-dry at 80° C.
C—Lower layer from B. Make up to 1,000 cc. with benzene. Adjust precipitation point to 29° C. and separate after standing overnight at 28° C.
D—Lower layer from C. Coagulate and mill dry. This is the least soluble fraction.
E—Upper layer from C. Evaporate and mill dry.
G—Liquid from A. Evaporate and wash three times with hot alcohol with stirring. Wash with warm acetone until the washings are colorless.
H—Insoluble from G. Vacuum-dry at 80° C.
I—Washings from G. Evaporate and vacuum-dry.

Compounds 1, 2, 3, and 4 were compared by this short method of fractionation. Compounds 2 and 3 were new batches of stock and the combined sulfur varied

TABLE VI

COMPARISON OF SULFUR DISTRIBUTION IN ACCELERATED AND UNACCELERATED COMPOUNDS

Fractions		D	E	F	H	I	Original
Compound 1	Grams	18.6	11.1	14.6	2.9	0.8	48.7
	% comb. S	1.69	1.70	1.67	2.37	6.07	1.92
Compound 2	Grams	10.2	11.2	23.0	2.4	1.4	48.5
	% comb. S	3.24	3.21	3.35	3.72	6.94	3.85
Compound 3	Grams	7.93	5.0	20.3	14.5	1.8	48.9
	% comb. S	4.46	2.34	1.61	1.54	5.27	2.38
Compound 4	Grams	11.9	9.6	18.2	4.3	1.1	45.0
	% comb. S	3.45	1.62	1.41	1.51	5.88	2.25
Compound 5	Grams	Could not be peptized.					
	% comb. S	—	—	—	—	—	0.34

slightly from that shown in Tables III and IV. The results, given in Table VI, show that both the aldehydeamine and di-*o*-tolylguanidine compounds had a non-uniform distribution of sulfur, while the unaccelerated vulcanizates 1 and 2 were more uniform. Compound 5, with only 0.34% of combined sulfur, could not be peptized.

No relation appears to exist between the physical properties of rubber and the ease of peptizing. The physical properties of compound 5 are much inferior to the properties of the other accelerated compounds which were readily peptized. If compound 5 did not peptize because the units were sufficiently well linked together by an efficient use of the small amount of combined sulfur, then the physical properties should have been improved to the same extent. Conversely, the units of the accelerated compounds with good physical properties should have been well linked together and the compounds should not have peptized.

Compound 5 failed to peptize because it was insufficiently solvated. If the units had been sufficiently separated by solvation, their relative positions could not have been maintained and the rubber could not have failed to dissolve. It is evident that the presence of combined sulfur is not sufficient to prevent solvation, since unaccelerated compound 2 contained high combined sulfur and yet peptized easily. The accelerated compounds 3 and 4 with good physical properties and high combined sulfur were somewhat more difficult to peptize than the unaccelerated compounds. These results could mean that solvation is retarded in proportion to the

degree of physical vulcanization and assisted by the presence of combined sulfur. According to such an explanation, compound 5 resists the action of solvents because of the good physical properties and extremely low combined sulfur.

An attempt was made to increase the sulfur content of compound 5 sufficiently to cause it to peptize. It was shown by Williams[12] that the physical vulcanization of rubber could be carried to such a point that the rubber would not peptize. For that reason it was necessary for the addition of sulfur to compound 5 to be carried out under conditions which would cause a minimum of physical vulcanization. The thoroughly acetone-extracted rubber which would not peptize was mixed intimately with 10% of its weight of sulfur on a small rubber mill and the mixture was vulcanized for 60 minutes at 142° C. The vulcanization was more rapid than that of a corresponding mix prepared with new rubber, and the combined sulfur was increased to 4.46%. The physical state of vulcanization was apparently in advance of that of the accelerated compounds 3 and 4. After acetone-extraction the rubber was brought into homogeneous solution by treatment for 72 hours at 98° C. with twice the usual volume of piperidine solution. In similar experiments the time required has sometimes been greater, and in some cases the rubber would not peptize completely. In all cases the revulcanized rubber was much more readily attacked. Complete success depends on maintaining the original physical properties during revulcanization.

Further addition of sulfur would not be expected to destroy thioether linkages. If treatment with free sulfur is able to break thioether bonds, then none of the compounds vulcanized with sulfur should contain thioether bonds, because free sulfur remains after vulcanization. Thioether sulfur is, however, known to be present in vulcanized rubber, and some of it may even serve to unite molecules of rubber, but it does not appear to constitute the force which holds the rubber units in the vulcanized condition.

It is unnecessary to assume the presence of bridges in rubber to account for the characteristic properties of vulcanized rubber. Fractions of peptized rubber form, by evaporation of their solutions, a film which has all the properties of vulcanized rubber. If sulfur contributes to the binding force it can be only through the medium of secondary forces. Stevens and Stevens[14] and Williams[12] have shown that it is possible to improve the physical properties of a vulcanizate to a considerable extent by the addition of soluble zinc salts and accelerator without altering the combined sulfur. The effect was suggested to be due only to a change in the colloidal structure of the rubber.

Rubber hydrocarbon is non-polar and contains a uniform field of force. Any chemical attack produces a non-uniform field and the units of rubber will attempt to shift their relative position to overcome the resulting uneven distribution of force. This change is spontaneous and not reversible. Any agent which because of its presence will assist this process will increase the accompanying change in physical properties. In the case of certain types of chemical attack by oxygen the resulting product is plastic. In case the attack is by sulfur it happens that plastic properties are lost and the rubber is vulcanized. Similar results are caused by a variety of chemical or physical means or, as Menadue has shown[15], even by the presence of certain fillers.

Combined sulfur is admittedly necessary for vulcanization with sulfur. The added sulfur serves only as an activating agent for the change which produces physical vulcanization, and the extent of the change depends on the presence of some material which assists the change. While existing information indicates that most of the sulfur is present in the thioether form, there is no evidence that it connects units of rubber or that such a process is necessary for vulcanization. The

entire lack of relationship between the amount of combined sulfur, the physical vulcanization, and the ability of the rubber to be peptized does not favor the sulfide linkage theory of vulcanization. If the vulcanized condition is caused by sulfur bridges, then the strongest rubber would also be the most resistant to solvents. The fact that the strongest rubber is also the most heterogeneous with respect to sulfur indicates that physical vulcanization is not produced by sulfur bridges between the molecules of rubber.

CONCLUSIONS

No direct evidence exists to support the sulfide linkage theory of vulcanization, which assumes that cross-linking of the molecules with sulfur would retain the elasticity and decrease the plasticity of the rubber.

The following facts do not favor the sulfide linkage theory of vulcanization:

(1) Vulcanized rubber can be peptized under conditions which do not appear to rupture a sulfide linkage.

(2) No direct relation exists between the physical properties of vulcanized rubber and the amount of combined sulfur.

(3) No direct relation exists between the ease of peptization and the physical properties of the vulcanizate.

(4) Combined sulfur appears to assist the solvation of rubber. Rubber vulcanized with thiuram disulfides in the absence of free sulfur has poor physical properties but peptizes with difficulty. An increase in combined sulfur without a corresponding improvement in physical properties assists solvation.

(5) Rubber having the best physical properties is also the most heterogeneous with respect to sulfur. The sulfide linkage theory would suggest that an even distribution of sulfur would produce the best physical properties.

(6) Fractions of peptized vulcanizates, on evaporation of their solutions, leave insoluble vulcanized films, which shows that linkage by means of primary forces is unnecessary for producing the vulcanized condition.

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THE INTERACTION OF MALEIC ANHYDRIDE WITH RUBBER *

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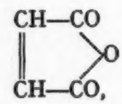
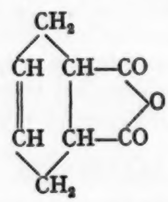
INTRODUCTION

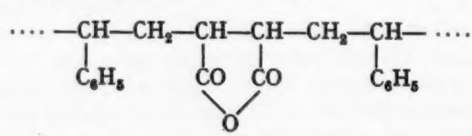
In recent years maleic anhydride,



has been extensively utilized by organic chemists both for synthetical operations and on account of its ready ability to form crystalline derivatives which serve to characterize certain types of unsaturated compounds. Its use in such reactions normally involves the so-called Diels-Alder condensation, a process whereby the maleic anhydride combines with compounds containing a conjugated carbon system of alternate single and double bonds, $-C=C-C=C-$, producing stable cyclic addition products. Thus, with butadiene, $CH_2=CH-CH=CH_2$, the reagent yields a crystalline compound, Δ^4-tetrahydro-*o*-phthalic anhydride[1]



Non-conjugated olefinic compounds, such as hydrocarbons of the ethylene series, do not react with maleic anhydride in such relatively simple fashion. On the other hand many cases are known of olefinic compounds which condense with maleic anhydride by a process of "additive heteropolymerization"[2]. This process is a special case of copolymerization, and has been defined as occurring between a polymerizable unsaturated substance, *e.g.*, styrene, and another unsaturated substance which does not itself readily polymerize (the latter in this case being maleic anhydride). Sometimes a catalyst is used to promote such reactions. The reaction products in these cases are amorphous open-chain polymers of high molecular weight, in which molecules of the anhydride are believed to be linked linearly with molecules of the other participant. Thus, styrene, $C_6H_5-CH=CH_2$, is thought to form polymeric chains of the type:



* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 56, pages 256-265.

Various heteropolymers of this kind are described in patent literature, *e.g.*, heteropolymers of maleic anhydride and vinyl acetate, which are formed in the presence of benzoyl peroxide[3].

The reaction products are regarded as having polymeric, open-chain, saturated structures; in all these respects they differ from Diels-Alder addition products. It may be pointed out, however, that even conjugated butadienoid hydrocarbons in some cases *e.g.*, α-methylbutadiene, yield a polymeric derivative in addition to the normal crystalline Diels-Alder addition product, and in other cases, *e.g.*, $\alpha\alpha$-dimethylbutadiene, yield a product which is wholly polymeric. Maleic anhydride, by itself, does not polymerize, even in the presence of a catalyst.

It was recently observed[4] that when masticated natural raw rubber and maleic anhydride, plus a little benzoyl peroxide (a common polymerization catalyst), are mixed together in benzene or toluene solution and the reaction mixture is heated for a few hours at about 100° C., interaction occurs, yielding a product which may be precipitated into alcohol, and which, when freed from solvent, is obtained as a white or pale yellow resin, possessing none of the elasticity of rubber. When maleic anhydride was used in the proportion of 1 molecule per C_5H_8 unit of rubber, the weight of benzoyl peroxide being equivalent to 10% of the rubber, the resinous derivative corresponded in yield and analysis to a product which might be formed by the combination of one-third of a molecule of maleic anhydride per C_5H_8 unit of rubber.

Rubber has not previously been reported to react with additive reagents of the maleic anhydride type. Since the reaction product has considerable technical and scientific interest, we have undertaken a detailed investigation of the process to elucidate as far as possible the conditions governing its formation and the nature of the changes involved. The present paper summarizes the principal results of our work to the time of writing.

FUNCTION OF THE BENZOYL PEROXIDE

When solutions of maleic anhydride and rubber are heated together in the absence of benzoyl peroxide no reaction occurs; on precipitation into alcohol the original rubber is obtained unchanged in appearance and shows no gain in weight. (It may be pointed out that alcohol-soluble substances present in the original rubber are removed by the precipitation process and cause a slight decrease in weight; this necessitates a small correction factor which we have applied when estimating the yields of our reaction products.) The same mixture of rubber and maleic anhydride, heated under the same conditions in the presence of a little benzoyl peroxide, readily yields a resinous product. The data presented in this paper demonstrate that under appropriate conditions, using quantities up to 8% of benzoyl peroxide (reckoned on the rubber), the weight of the resinous derivative may be more than 100% greater than that of the original rubber. Hence it may be concluded that the essential feature of the reaction is the addition of maleic anhydride to the rubber molecule; although the benzoyl peroxide probably to some extent interacts concurrently with the rubber, its function would appear to be essentially catalytic.

It is of course well known that benzoyl peroxide will itself add to rubber[5], and may be employed as a vulcanizing agent[6]. However, we have found, using up to 8% of benzoyl peroxide in a toluene solution of rubber, that under conditions typical for our experiments (18 hours' heating at 100° C.) precipitation into alco-

hol gives a very tacky but still fairly rubbery product, in no way resembling the resinous derivatives produced when maleic anhydride is present in the reaction mixture.

Further observations exclude the possibility that our reaction products are merely mixtures of unchanged rubber with a maleic anhydride polymer generated under the influence of the peroxide. When, for instance, maleic anhydride and benzoyl peroxide were heated together in toluene solution under the usual reaction conditions, mixed with rubber at the end of the heating process, and then stirred into alcohol, only unchanged rubber was precipitated. When the same proportions of rubber, maleic anhydride and benzoyl peroxide were all mixed together before heating, then under the usual reaction conditions a resinous derivative resulted.

INFLUENCE OF VARYING EXPERIMENTAL CONDITIONS

We have found that the formation of the maleic anhydride addition compound is accompanied by a reduction in unsaturation of the rubber molecules (see later). On the hypothesis that each maleic anhydride molecule may interact with one C_5H_8 unit, it may be calculated that complete saturation of rubber would lead to an increase in weight of 144%. Working in solution under varying experimental conditions, it has been found possible to obtain an extensive series of reaction products, exhibiting a gradation in their composition and properties. At the lower end of the series are products which are but slightly heavier than the original rubber and differ from it but little in physical characteristics, and at the upper end are intractable resinous substances more than 100% heavier than the original rubber. The maximum gain in weight so far recorded is of the order of 120%.

The nature and the yield of the reaction product is influenced by the relative proportions of the reactants, by the amount of benzoyl peroxide, by the nature of the solvent and by the temperature and time of reaction. These factors will be considered in turn.

(1) *Proportion of Benzoyl Peroxide.*—The extent to which benzoyl peroxide is effective in promoting the interaction of maleic anhydride and rubber has been found to depend to a considerable extent on its proportion. The influence of this factor may be illustrated by reference to a series of experiments in which a varying quantity of peroxide was employed under otherwise standard conditions. Toluene solutions of 10.0 grams of maleic anhydride and 7.0 grams of masticated rubber, *i.e.*, 1 molecule of anhydride per C_5H_8 unit, were mixed together, and a known quantity of peroxide was added, the rubber concentration being 3% by weight of the mixture. In each case the mixture was heated for 18 hours in a bath maintained at 90° C., and then slowly added, with brisk stirring, to four times its volume of alcohol, which precipitated the product and removed unchanged anhydride. The precipitate was isolated, washed, and dried to constant weight at 70° C. *in vacuo*. The effect of varying the amount of catalyst on the yield and nature of the product is illustrated in Table I.

It will be observed that an increasing degree of addition is accompanied by loss of coherence and the replacement of rubber-like properties of resinous characteristics. In two more extreme cases, in which 20% and 30% of benzoyl peroxide were employed, the products were resins exhibiting an increase in weight of 103% and 129%, respectively.

(2) *Maleic Anhydride/Rubber Ratio.*—The data in Table I indicate that in benzene or toluene solution, using moderate amounts of benzoyl peroxide, two-

thirds or more of the maleic anhydride which was employed failed to react. If a very considerable excess of maleic anhydride is used, under standard experimental conditions, a larger amount will enter into combination, presumably owing to the influence of its increased relative mass, but this improvement in yield is by no means proportional to the increase in the anhydride/rubber ratio. The effect is illustrated in Table II, which refers to experiments conducted for 18 hours at 90° C. in toluene solution with 10% of benzoyl peroxide.

Table I

(7 Parts Rubber + 10 Parts Anhydride)

Amount of benzoyl peroxide relative to the rubber.	1%	3%	7%	10%
Nature of the precipitate.	Coherent, white rubbery mass, collecting on the stirrer.	Coarse, fibrous, white precipitate.	Finely divided, white precipitate.	Finely divided, white precipitate.
Nature of dried product.	Very tough, rubbery product; non-tacky.	Tough, somewhat fibrous product, intermediate between rubber and resin.	Brittle, pale yellow resin.	Brittle, pale yellow resin.
Weight of product relative to the rubber.	12% increase.	24% increase.	52% increase.	53% increase.

Table II

(10% Benzoyl Peroxide)

Number of mols. of maleic anhydride per C_5H_8 unit of rubber.	1.16	2.32	4.62
Weight of product relative to the rubber.	52% increase.	69% increase.	88% increase.

Table III

(8% Benzoyl Peroxide)

	(a)	(b)	(c)	(d)	(e)
Number of mols. of maleic anhydride per C_5H_8 unit of rubber.	0.50	0.25	0.20	0.13	0.07
Weight of product relative to the rubber.	35% increase.	27% increase.	15% increase.	13% increase.	9% increase.

The dried products were all yellow resins.

At the other end of the scale we have investigated the effect of reducing the anhydride/rubber ratio well below unity. The data in Table III were obtained by using 8% of catalyst (reckoned on the rubber), in toluene solution, and heating for 18 hours at 100° C.

The product (*a*) does not adhere to the stirrer during precipitation, but separates as a coarse white fibrous solid, which when dried may have a somewhat

asbestos-like quality. The series (*b*) to (*e*) collect partly or entirely round the stirrer during precipitation, and are superficially rubber-like in appearance. They are particularly interesting because, although they contain only a relatively small amount of maleic anhydride, they are very different from rubber, being extremely tough yet retaining considerable elasticity. They are not tacky.

(3) *Influence of the Solvent.*—It is obviously necessary that the solvent selected for the study of the reaction should dissolve maleic anhydride as well as rubber. Benzene, toluene, and xylene are very satisfactory in these respects, but the data which we have presented show that in these solvents the addition process does not readily go very far towards the hypothetical limit corresponding to complete saturation. Certain other liquids are less satisfactory as solvents, but have been found to give a higher degree of addition.

The course of the reaction in carbon tetrachloride is interesting. Although this is a suitable solvent for rubber, maleic anhydride dissolves in it only sparingly. When the reaction mixture is heated, the addition product separates as a spongy, fibrous solid, usually pinkish, and readily separated by filtration. Addition of the filtrate to alcohol fails to precipitate any further quantity of product. Using rubber and maleic anhydride in the ratio of 1 C_5H_8 unit per 2 molecules, the amount of the benzoyl peroxide being 8% and the concentration of the solution being less than 1% (both with reference to the rubber), we have obtained, after two days' heating at 73° C., a product 117% heavier than the original rubber. This figure is equivalent to 80% of the hypothetical figure of 144%, which we suggested might approximately correspond with complete saturation of the rubber. The dried product is a hard resin.

The behavior of chloroform as a solvent is very different from that of carbon tetrachloride. It dissolves rubber readily and maleic anhydride with great ease. In view of its relatively low boiling-point, the reaction was attempted at 55° C. Nothing separated from the solution during a heating period of two days. When the mixture was precipitated into alcohol there appeared a small quantity of sticky material, possibly due to benzoyl peroxide, but if any derivative had been formed it was apparently too soluble to come down from the chloroform-alcohol mixture.

Both decalin (decahydronaphthalene) and cyclohexane have been satisfactorily employed as solvents. Using in each case 1 molecule of maleic anhydride per C_5H_8 unit, and 8% of peroxide, the former solvent gave a brown resin, representing a 60% increase in weight, after 16 hours at 155° C., and the latter gave a pale yellow resin, representing a 70% increase in weight, after 21 hours at 72° C.

(4) *Influence of Concentration: Gelling.*—The first apparent effect of heating a solution of rubber containing benzoyl peroxide is a considerable decrease in viscosity. Heating a mixed solution of rubber, maleic anhydride and benzoyl peroxide has a similar effect. However, it frequently happens that during the heating process gelling occurs, sometimes to a small extent only, and sometimes to a pronounced degree. From these gels the addition product may often be isolated by allowing the gel fragments to stand in alcohol, when they are soon replaced by husks of a firm, fibrous, solid product. If the gel is very stiff, the derivative is best isolated by subjecting it to steam distillation.

It must be emphasized, however, that gel formation is not to be regarded as a necessary sign and accompaniment of the reaction between rubber and maleic anhydride. Practically all the solutions which provided the data tabulated above were entirely free from gelling. The likelihood of gelling is largely dependent on the concentration of the solution. It is to be expected when the concentration

exceeds about 3% by weight. The concentration of benzoyl peroxide is also an important factor. We observed, for instance, that a 5% solution of rubber in toluene is gelled at 100° C. by amounts of benzoyl peroxide between 2% and 10% (referred to the rubber), but not by 1%. It is likely, too, that gelling is more prone to occur in some solvents than in others.

(5) *Time and Temperature of Heating.*—The addition process is apparently quite rapid. In aromatic hydrocarbon solvents the reaction appears to reach its limit in a few hours. In carbon tetrachloride the derivative begins to be precipitated fairly soon after heating begins. No pronounced improvement in yield has been observed to occur when the reaction is conducted at a temperature higher than the customary 80° or 90° C.

CHARACTERISTICS OF THE ADDITION PRODUCTS

The properties of the derivatives vary according to the proportion of combined maleic anhydride which they contain. It has already been pointed out how a gradual transition may be observed from tough but still fairly rubbery products, containing only a few units per cent. of anhydride, through fibrous substances, to hard and brittle resins, which contain more than a third of their weight of combined maleic anhydride and possess none of the typical physical characteristics of rubber. Corresponding to increasing maleic anhydride content, an increasing fineness in particle size and an increasing loss of coherence in the product are to be observed during precipitation. This progressive modification of physical properties is an outstanding feature of the reaction.

Pronounced differences are to be observed between the solubilities of the derivatives compared with that of the original rubber. The derivatives are more readily brought into solution when freshly precipitated than when dry. Generally speaking, they go into solution much less easily than rubber does, particularly when the content of combined maleic anhydride is large; a very high anhydride content makes them very intractable. At the same time the introduction of maleic anhydride into the rubber molecule makes the derivatives more responsive to those solvents which dissolve maleic anhydride itself. For instance, boiling ethyl alcohol may dissolve the derivatives after several hours of heating, sometimes completely and sometimes to a limited extent. There are indications that the process of dissolution may be accompanied by esterification of the anhydride groups in the product. Alcoholic solutions of an alkali have been successfully used for dissolving the derivatives, as have also solvents of a basic nature, such as aniline.

The derivatives appear to be quite stable at moderately high temperatures and do not readily soften. However, in this as in other respects further investigation is needed before the characteristics of the substance can be more fully described.

ANALYTICAL DATA

Analyses carried out on a series of products containing various amounts of maleic anhydride, carefully freed from all solvent but not otherwise purified, gave values for carbon and hydrogen of the expected order. However, the values, particularly those for carbon, were usually less by 2% or more than the figures calculated on the assumption that the observed increase in weight was due solely to the addition of maleic anhydride to rubber hydrocarbon, and that the original rubber could be represented as $(C_5H_8)_n$. These discrepancies might be due to the presence of oxygen-containing or nitrogenous substances in the original masti-

cated rubber, the occurrence of secondary reactions involving the benzoyl peroxide, the retention of part of the reaction product in the alcohol-benzene mixture during precipitation, and the occurrence of hydration or esterification of the anhydride groups during heating or precipitation. The discrepancies were biggest for the derivatives which represented the greatest increase in weight.

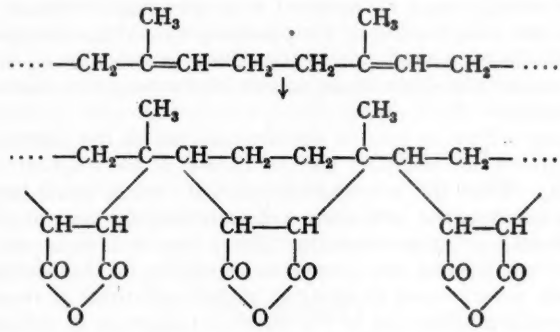
It is not very easy to obtain unsaturation values for the derivatives because of their insoluble nature. Accordingly, we are examining the iodine values of samples taken direct from a typical reaction mixture heated in benzene solution. For this purpose we have employed the method of Kemp[7], using the Wijs reagent. A correction is necessary on account of the benzene, but this is reduced if the benzene has been previously purified by heating it with maleic anhydride. On the other hand, the iodine value for maleic anhydride is found to be practically zero, and so this substance does not interfere when present in the unchanged state. Tests have been carried out on a benzene solution containing rubber, maleic anhydride and benzoyl peroxide (1.489, 2.135 and 0.118%, respectively, of the total solution), which was heated for 18 hours at 90-95° C. Samples from this solution gave an average iodine value of 189 (referred to 100 grams of rubber). By contrast, a similar solution, heated under the same conditions but containing no benzoyl peroxide, gave an average iodine value of 324. Hence the addition reaction brought about by benzoyl peroxide reduced the unsaturation value of the rubber by about 42%. Working on the assumption that the reaction involves the saturation of the double bond in 1 C_5H_8 unit for the addition of each maleic anhydride molecule, it could be readily calculated, knowing the weight of product obtainable by precipitation of the reaction mixture, that the hypothetical reduction in the unsaturation value should be about 37%. There is a sufficient degree of agreement between this and the experimental figure to support the view that an addition reaction occurs between maleic anhydride molecules and double bonds of the rubber.

DISCUSSION

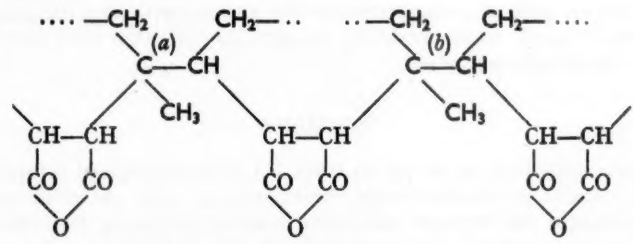
Benzoyl peroxide is well known to be a powerful activator of polymerization process. Its function in the present instance might be similarly interpreted: it stimulates the reactivity of the double bonds in rubber sufficiently to bring them into reaction with maleic anhydride, which in its absence will not combine with them. The use of this catalyst in promoting heteropolymerization reactions may be cited, *e. g.*, maleic anhydride and vinyl acetate[3], but it will be observed that whereas in heteropolymerization processes a polymerizable unsaturated substance like vinyl actetate or styrene is normally involved, rubber is already a high-molecular polymeride. It is a difficult matter to suggest with any degree of certainty what type of structure may result from the combination of rubber and maleic anhydride. In the first place, no very exact information is available concerning the structure of polymeric materials produced by the interaction of maleic anhydride with the simpler olefinic substances concerned in the heteropolymerization processes which have so far been studied, and even if such knowledge were available, the complicated molecule of rubber would not necessarily present an analogous case. In the second place the reaction with rubber possibly follows more than one course.

However, drawing an analogy between the addition reaction with rubber and the supposed course of known heteropolymerization reactions which involve maleic anhydride, it may be suggested that the anhydride becomes linked either (1) between neighboring double bonds in the same rubber molecule, or (2) between double bonds in different rubber molecules which lie adjacent, or (3) be-

tween double bonds in different sections of the same molecule which happen to have become adjacent owing to the twisting of the molecule. In case (1) structures of the following type might result:



and in cases (2) or (3) structures of the type:



where the C_5H_8 groupings (*a*) and (*b*) represent fragments from adjacent rubber chains or from different sections of the same rubber chain which have become adjacent. If cross-linkages between separate molecules are formed as in case (2), they will produce molecular systems of great complexity, which might be expected to be highly insoluble. Possibly all the above modes of linkage are present together in the addition product.

Alternatively, but much less likely, there is the possibility that maleic anhydride adds on to double bonds in rubber to produce four-membered rings, or even becomes attached by single bonds with migration of hydrogen. There is a remote possibility too that migration of double bonds might occur to some extent in rubber molecules under the influence of the catalyst, producing conjugated systems to which maleic anhydride might add in the manner of an ordinary Diels-Alder condensation. Against this view may be set the fact that we have not obtained derivatives when maleic anhydride is replaced by *p*-benzoquinone, which also readily condenses with conjugated compounds.

It is evident too that benzoyl peroxide may become involved in reaction apart from its catalytic function, since it is known to act towards rubber both as an additive and as an oxidizing reagent. Such processes might proceed either as intermediate or as concurrent secondary reactions to the main process of maleic anhydride addition. It should be remembered, however, that whereas rubber and benzoyl peroxide alone yield an extremely sticky product, the addition of only

a very small quantity of maleic anhydride to the reaction mixture is sufficient to give instead very tough materials which are not tacky.

A further possibility suggests itself; the activated rubber molecules may perhaps polymerize, or may cyclize or undergo other internal rearrangements. However, although such changes may be involved to a very limited extent, our evidence indicates that the main feature of the process is an addition reaction, the maleic anhydride molecules condensing on to the rubber, possibly on to, or between, the unsaturated centres of a single chain, or possibly between the unsaturated centres of adjacent chains.

In conclusion, it may be pointed out that the aim of the present investigation has been to explore the conditions and mechanism of the reaction rather than its technical utility. From the technological point of view it would be interesting to look for other catalysts and to find ways of decreasing the amount of solvent used, or even eliminating it. It is noteworthy that a very wide range of derivatives is available, their composition and properties depending on the reaction conditions. Moreover, only a very small quantity of maleic anhydride is required to bring about considerable modification in the physical properties of rubber.

It may be suggested too that other organic compounds, related in their structure to maleic anhydride, may be found to add to rubber in a similar way. It is evident that, once maleic anhydride or similar compounds have been incorporated into the rubber molecule, they provide the system with reactive groups, *e.g.*, carbonyl or carboxyl, which might be brought into reaction with other reagents to modify the structure further.

SUMMARY

(1) Maleic anhydride is known to react (*a*) with conjugated compounds, *e.g.*, butadiene, usually producing simple cyclic systems, and (*b*) with unsaturated olefinic substances like styrene and vinyl acetate, producing long-chain heteropolymers. It is now demonstrated that maleic anhydride, under the influence of a little benzoyl peroxide, will react in solution with rubber on heating, yielding a variety of tough, fibrous or resinous products.

(2) It is shown that these derivatives are not produced by the action of maleic anhydride alone or of benzoyl peroxide alone, nor are they mixtures of rubber and maleic anhydride polymer.

(3) As a result of the reaction, rubber has been found to undergo an increase in weight ranging from a few per cent up to about 120%, according to experimental conditions. The corresponding derivatives differ greatly from rubber in mechanical properties, and range from products which are tough, rubbery and non-tacky, to hard and brittle resins.

(4) The effect of varying the quantity of benzoyl peroxide between 1% and 10%, and of using greater excess, is demonstrated.

(5) The effect of varying the maleic anhydride/C_5H_8 ratio between 0.05 and 5 is demonstrated.

(6) It is is shown that the nature of the solvent greatly influences the extent of reaction. The use of benzene, toluene, xylene, carbon terachloride, chloroform, decalin, and cyclohexane is discussed.

(7) The influence of concentration and the occurrence of gelling have been investigated.

(8) The derivatives are very different from rubber in their solubility characteristics.

(9) Determination of the iodine number of the reaction mixture shows that a loss of unsaturation in the rubber occurs during the reaction, this loss approximately corresponding with the disappearance of one double bond for each maleic anhydride molecule adding.

(10) It is suggested that the process is essentially a catalyzed addition reaction, the maleic anhydride probably forming links between double bonds either in the same chain or in adjacent molecules, the double bonds thereby becoming saturated. Intermediary or secondary reactions, such as oxidation or addition by benzoyl peroxide or internal rearrangements in the rubber molecule occurring to a minor extent, are not altogether excluded.

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AN X-RAY STUDY OF RUBBER HYDROCHLORIDE *

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INTRODUCTION

The utilization of rubber has been a continuous challenge to our knowledge and understanding of the raw material which nature has provided. At every turn in the long road of development leading to the innumerable applications of rubber for present day needs, there has occurred the necessity of taking a substance which will not do and modifying it, sometimes a little, sometimes a great deal, to make it serve a desired purpose. In this tradition, there has been in recent years an increased interest in chemical modifications of rubber hydrocarbon.

The addition product of rubber and hydrogen chloride, known as rubber hydrochloride, was studied by Weber[1] in 1900. He passed hydrogen chloride through a solution of rubber in chloroform and precipitated the product by pouring the solution into alcohol. The early concern with rubber hydrochloride lay in using it as a means for investigating the chemical constitution of rubber.

Harries[2, 3] removed hydrogen chloride from rubber hydrochloride by heating it in a tube with pyridine at 125° to 135° C. The resulting product, which he termed α-isorubber, was useful in his extensive researches on the structure of rubber. Staudinger and Widmer[4, 5], by reacting a solution of rubber hydrochloride with zinc dust, prepared a rubber derivative having half of the unsaturation of rubber. This was designated as monocyclorubber. References to other chemical investigations on rubber hydrochloride are given in Memmler's *Science of Rubber*[6].

Rubber hydrochloride did not find its way into the arts to any extent until within the last few years. It has now been shown to have certain valuable applications, especially when used as a film[7]. There is practically no information in the scientific literature on its physical properties[35] or x-ray structure. Mark and von Susich[8] have reported that its x-ray diagram is a broad amorphous halo corresponding to a spacing of 5 Å. Meyer, von Susich and Valko[24] also say that it is amorphous. Both amorphous and crystalline rubber hydrochlorides have been described in U. S. patents[9].

X-RAY DIAGRAM OF RUBBER HYDROCHLORIDE IN RELATION TO THAT OF RUBBER AND DERIVED HYDROCARBONS

The x-ray patterns were secured with a General Electric x-ray diffraction unit equipped with a Philips Metalix copper anode tube operated at 35,000 k.v.p. and 27 milliamperes. The new Agfa non-screen x-ray film was found to cut the exposure times in half and was used throughout.

The amorphous x-ray diagram of rubber has been frequently published[10, 11] but is given here, Figure 1, for convenience of reference. The diameter of the amorphous halo indicates an intermolecular spacing of 5.0 Å, characteristic of a branched chain[12]. To demonstrate the alteration of this diagram as hydrogen chloride is added to the rubber, a series of rubber hydrochlorides with increasing concentrations of chlorine was prepared. Hydrogen chloride from a sulfuric acid-hydrochloric acid generator was passed into a 2% by volume solution of petroleum

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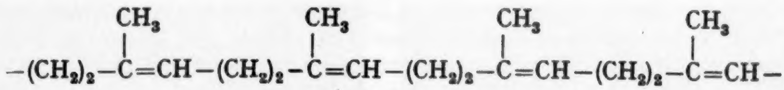
ether diffusion rubber[13] in chloroform. The solution was kept at a temperature of 4° C. and stirred. Samples of the solution were withdrawn at intervals and precipitated with alcohol. Each precipitate was cut into small pieces and extracted with alcohol for 48 hours and then dried *in vacuo*. The x-ray diagrams and the chlorine contents, determined by analysis, are given in Figures 2, 3, 4 and 5. It is evident from these diagrams that the partially reacted rubber hydrochlorides are not, as regards their x-ray structure, a mixture of rubber and the product of complete hydrochlorination. The effect on the x-ray diagram, caused by the first addition of hydrogen chloride, Figure 2, is the appearance of a very small ring which barely passes the central lead bead. It may not be visible in the reproduction of the film. The calculated spacing for this ring is approximately 40 Å. The next effect (Fig. 3) is the occurrence of an amorphous blackening on the film (white in the reproduction) in the center of the diagram which would also be attributed to rather large molecular spacings. On the films, this blackening can be seen to include a broad ring, spacing 10.5 Å, and a sharper ring, spacing 17.5 Å. The large spacing of 40 Å also is registered. More will be said about the significance of this inner blackening later. The amorphous halo of rubber is still present but is perceptibly narrower.

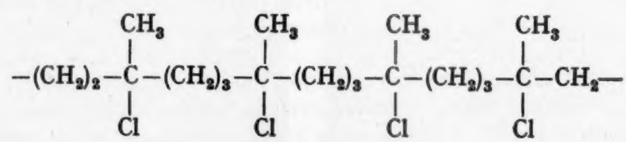
As the chlorine content is further increased (Fig. 4), there is a remarkable shift in intensity between the outer and inner parts of the pattern. Sharp crystalline rings appear in the approximate position previously occupied by the amorphous halo, but are relatively less intense than the broad inner ring. The last diagram of the series (Fig. 5), shows the full development of a system of crystalline rings. It will be noted that the final chlorine content, 31%, is lower than the theoretical value of 34%. This is characteristic of the reaction. Figures 6 and 7 are the crystalline diagrams of frozen rubber and balata respectively, for comparison.

The removal of hydrogen chloride from rubber hydrochloride by Harries and by Staudinger was mentioned at the outset. X-ray diagrams of these hydrocarbons should also have a bearing on this study. Samples were prepared using the rubber hydrochloride which gave Figure 5 and following the procedures already referred to. The α-isorubber was dark and rather plastic, the monocyclorubber light in color but hard and friable. Chlorine content of the former was 0.68%, of the latter 0.47%.

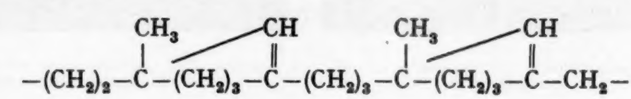
The generally accepted chemical representation for a rubber molecule is a long chain of isopentene groups, as shown below:



Addition of hydrogen chloride should give:



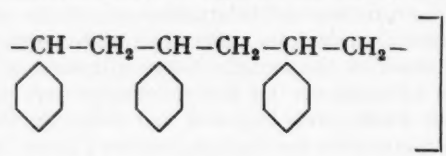
Staudinger regarded the monocyclorubber as:



Harries' speculations on the structure of α-isorubber are reviewed in Memmler[14].

From the chemical standpoint, rubber is a terpene. It belongs to this extensive family of hydrocarbons, built up with C_5H_8 (isoprene) groups, which includes the predominant part of the essential oils. By processes still not entirely understood[15], the isoprene group is synthesized in plant and animal life into a wide variety of complex compounds. It is a structural unit in vitamin A[16]. Many of the terpenes are cyclic or polycyclic compounds and, in fact, a straight chain structure like that of rubber is rather the exception than the rule. This tendency toward cyclization can be demonstrated in reactions of the rubber hydrocarbon. Thus, on pyrolysis, rubber gives off large quantities of dipentene, a monocyclic terpene[17].

The x-ray diagrams of monocyclorubber and α-isorubber are shown in Figures 8 and 9. α-Isorubber gives a halo of the same diameter as that of rubber, but the halo for monocyclorubber is smaller, representing a spacing of 5.7 Å. In this connection it is of interest to present the x-ray diagram (Fig. 10) of another rubber derivative which is considered to be a polycyclorubber. The preparation of these polymers has been described by Bruson, Sebrell, and Calvert[18]. Boron trifluoride was used as the cyclizing agent for the specimen of Figure 10. The spacing responsible for the amorphous halo is 6.0 Å. The decrease in the diameter of the amorphous halo for rubber (Fig. 1) on cyclization (Figs. 9 and 10), and the inner intensity of diffraction during hydrochlorination (Fig. 3), is reminiscent of the inner polymerization ring which Katz[12] has observed for polystyrene. In that case there are two rings, the outer amorphous halo of the monomer persisting. Katz has suggested that this larger spacing, 10 Å, which appears on the polymerization of polystyrene may be caused by the fact that the benzene rings attached to the long chain molecules serve to separate the chains, thus.



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By analogy, the larger spacing for cyclized rubber may be connected with the closed rings which are formed. In spite of the larger interatomic distance indicated by the x-ray diagrams, the density of the polycyclorubber is greater than that of rubber.

Referring back to Figure 3, it was observed that an early effect of the addition of hydrogen chloride was to cause an inner blackening of the diagram showing the occurrence of larger spacings. It has been known for many years that the addition of small quantities of hydrochloric acid caused a decrease in the viscosity of rubber solutions. This has usually been ascribed to a breaking up of the rubber molecules into smaller chains. The viscosity of dilute rubber solutions has been employed by Staudinger as a measure of the molecular weight[19]. The possibility that decreases in the viscosity of rubber solutions caused by acids, accelerators and other agents may be an indication of cyclization should be considered. In the case of rubber hydrochloride, there is further evidence for partial cyclization in the fact that the hydrogen chloride which can be added is less than the theoretical amount. Moreover, the tendency for the hydrohalides to cause cyclization is exemplified by the reaction of rubber with hydrogen fluoride. In this case an addition product, if formed, is unstable and the rubber is cyclized.

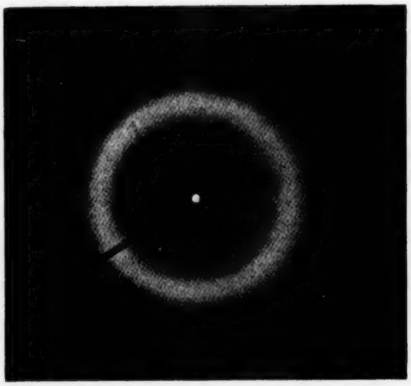

FIG. 1.—Unstretched rubber. Film-specimen distance 50 mm.

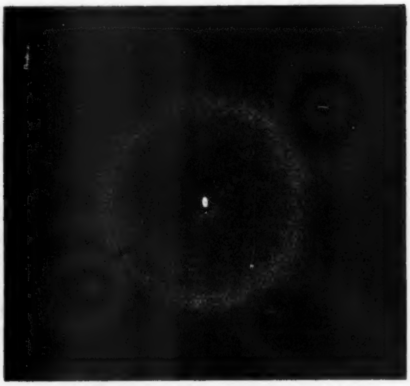

FIG. 2.—Rubber hydrochloride, 0.10% chlorine. Film-specimen distance 50 mm.

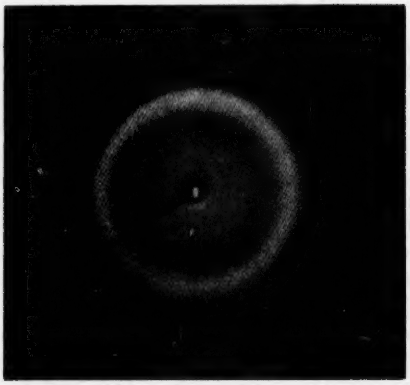

FIG. 3.—Rubber hydrochloride, 25.6% chlorine. Film-specimen distance 50 mm.

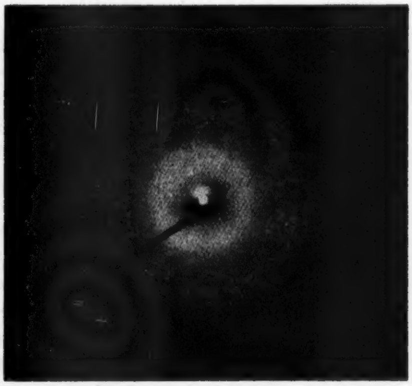

FIG. 4.—Rubber hydrochloride, 30.0% chlorine. Film-specimen distance 50 mm.

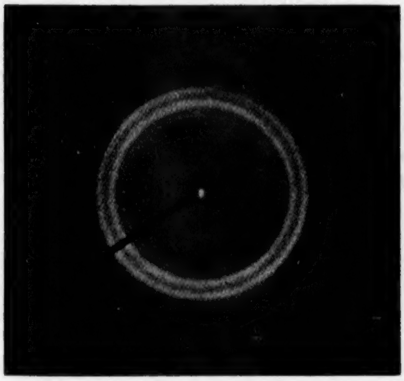

FIG. 5.—Rubber hydrochloride, 31% chlorine. Film-specimen distance 50 mm.

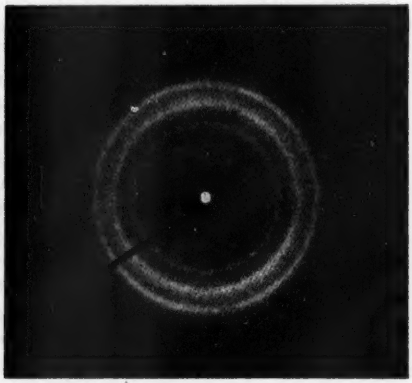

FIG. 6.—Frozen rubber. Film-specimen distance 50 mm.

X-RAY DIAGRAMS OF RUBBER HYDROCHLORIDE PREPARED BY SEVERAL METHODS

Samples of rubber hydrochloride were prepared in a number of ways and their x-ray diagrams examined. In reference[9], it is stated that amorphous rubber hydrochloride can be prepared by reacting solid rubber with hydrogen chloride at a low temperature, $-85°$ C. The only sample of such material which was available for this work was a year old. During that time it had been stored in the refrigerator. This specimen gave crystalline rings like those in Figure 5. There is still the possibility that the material is amorphous for some time after it is first prepared, since the conditions of the reaction are such that the molecular rearrangement required for crystallization may be very slow. The chemical explanation offered[9] for an amorphous structure is improbable. The amorphous structure is attributed to an asymmetrical formula, as shown below:

$$\begin{array}{ccccccccccccccc} & & CH_3 & & & & & & & & CH_3 & & & & \\ & & | & & & & & & & & | & & & & \\ -CH_2 & - & C & - & CH & - & CH_2 & - & CH_2 & - & C & - & CH & - & CH_2- \\ & & | & & | & & & & & & | & & | & & \\ & & H & & Cl & & & & & & Cl & & H & & \end{array}$$

The occurrence of such an addition is a violation of Markownikoff's rule which has been abundantly verified for hydrogen chloride[20].

Memmler[3] states that, in unpublished work, Pummerer and Stärk hydrochlorinated gel rubber and that the product resembled that from total rubber. It seemed of sufficient interest to secure the x-ray diagram of the gel rubber hydrochloride. For this purpose a sample of purified gel rubber, prepared by W. H. Smith at the Bureau of Standards[21, 22], was swelled in a large excess of chloroform. When hydrogen chloride was passed in, the rubber very soon went into solution and the reaction proceeded in the normal manner. The product resembled the hydrochloride of sol rubber in every superficial way. The x-ray diagram of the gel rubber hydrochloride was the same as Figure 5.

When rubber is reacted with hydrogen chloride in a solvent in which rubber hydrochloride is insoluble, rubber hydrochloride is precipitated out as the reaction proceeds. The x-ray diagram of rubber hydrochloride prepared in this way in a solvent mixture of ethyl ether and gasoline gave the normal crystalline pattern.

Harries[23] hydrochlorinated gutta-percha. Using purified balata instead of gutta-percha, a similar reaction was carried out in chloroform solution at 4° C. The x-ray diagram of hydrochlorinated balata is shown in Figure 11. It is very similar to Figure 3. No crystalline rings appear, but the halo is rather narrow. The original crystalline structure of the balata (Fig. 7) has disappeared entirely. Since Figure 11 has the appearance of the partially hydrochlorinated rubber, the reaction with balata was continued for 140 hours, but the diagram did not change. This difference in the x-ray structure of rubber hydrochloride and balata hydrochloride may be taken as more evidence that, although the addition of hydrogen chloride to straight chain molecules may represent the reaction in a general way, there are complications, such as partial cyclization which has been previously discussed, which may cause marked effects on the colloidal structure and probably the x-ray diagram. The failure to obtain the normal pattern of rubber hydrochloride for balata hydrochloride is only a negative result, however, and should not carry as great significance as a positively different crystalline pattern.

The solution of balata hydrochloride had a very low viscosity compared with solutions of rubber hydrochloride. To determine whether a rubber hydrochloride which gave a low viscosity solution would still give a crystalline diagram, a sample

of rubber hydrochloride was prepared using excessively masticated pale crepe rubber. This rubber hydrochloride gave a strong, crystalline diagram.

Data on the various hydrocholorides examined are given in Table I. The viscosities were determined in commercial chloroform containing a small percentage of alcohol as a preservative.

TABLE I

Rubber hydrochloride	% Chlorine	Specific viscosity (0.2% by volume in chloroform)
From sol rubber	31.2	.88
From gel rubber	31.0	.67
Sol rubber reacted with liquid HCl	27.2	.69
Milled crepe reacted in ethyl ether-gasoline	30.5	.91
From highly masticated crepe	31.0	.24
Balata hydrochloride	30.8	.17

THE OCCURRENCE OF THE CRYSTALLINE STRUCTURE

In the work here recounted, the rubber hydrochloride was the reaction product described in the first section, containing about 31% of chlorine. The effect of temperature on the crystalline pattern was investigated. It was found that the crystalline pattern passed into an amorphous one at a temperature of about 110° C. The x-ray diagrams are shown in Figures 12 and 13. In Figure 12, the sample was held at 105° C. during the exposure and in Figure 13 at 115° C. In all these experiments at higher temperatures, there is every reason to believe that the time intervals were short enough so that no appreciable decomposition occurred. The crystalline pattern, after heating to 115° C., failed to reappear in 24 hours at room temperature.

After 48 hours, the pattern of Figure 14 was obtained. Crystalline rings are present but also an amorphous halo. Within the accuracy of the measurements, these rings correspond to spacings in the normal crystalline pattern. Therefore the interpretation of Figure 14 is that the specimen was not homogeneous. Some of it had recrystallized, but some had remained amorphous.

A specimen heated at 120° C. just long enough to assure uniform temperature, failed to recrystallize after several weeks at room temperature. It was found, however, that the crystalline diagram returned when the sample was moistened with chloroform and dried at 70° C. Apparently the solvent and moderate temperature loosened the molecular structure sufficiently to permit crystallization.

When rubber hydrochloride is spread as a film from chloroform solution, for instance, and the solvent evaporated at 70° C., the film is exceedingly soft and plastic for several days. X-ray diagrams of this freshly prepared film, however, gave crystalline rings. Even when 10% of the solvent was left in the film, the crystalline rings appeared without evidence of broadening. There was, however, an increased intensity in the centre of the diagram. This effect is shown in the diagrams of Figures 15 and 16. In this case, acetylene tetrachloride was used as solvent because it was less volatile than chloroform and the loss of solvent during the exposure was less, although the same general results were obtained with chloroform. In Figure 15, the rubber hydrochloride contained about 40% by volume of solvent. The crystalline rings are absent entirely but a broad ring corresponding to a spacing of 10.7 Å occurs. For Figure 16, the solvent was reduced to 25% by volume. The inner ring is still strong, but the crystalline rings are sharp and intense. The absence of either crystalline rings or an amorphous halo in Figure 15 is a very striking result. It was suspected that this might be associated in some way with the high absorption of the acetylene tetrachloride and chloroform for the

CuK_α radiation. A diagram like that of Figure 15 was obtained for rubber containing 40% acetylene tetrachloride, but for rubber and xylene the diagram showed a strong amorphous halo. It is still somewhat of an open question, therefore, whether the highly chlorinated solvents cause sufficient disturbance of the intermolecular spacings to result in the disappearance of the amorphous halo. The exposure for Figure 15 was at least twice as great as for that of Figure 16.

The persistence of the crystalline pattern of rubber hydrochloride in the presence of an appreciable volume of solvent is in marked contrast to the effect of solvent on the crystalline diagram of stretched rubber. In this case, the solvent has the same effect as a rise in temperature and causes the spots to disappear[25].

The results with rubber hydrochloride testify to the strength of the internal orienting forces. The presence of the solvent, instead of causing an increased thermal agitation and disrupting the lattice, appears to act as a lubricant and assist the orienting forces of the rubber hydrochloride molecules. Only when sufficient solvent is present to separate the molecules beyond the range of these forces does the material fail to crystallize. These facts also fall in line with the insolubility of rubber hydrochloride in most rubber solvents. Due to the persistence of the crystalline structure, it should be possible to secure oriented diagrams by stretching rubber hydrochloride containing solvent.

The addition of a plasticizer to rubber hydrochloride had small effect on the x-ray diagram, as may be inferred from the effects with solvents. Figure 17 was taken with a sample containing 15% of dibutyl phthalate, the temperature of the exposure being 110° C. At 115° C., Figure 18, the crystalline rings have become quite diffuse. The plasticizer increases the relative intensity of the diffraction in the central portion of the diagram.

THE LATTICE SPACINGS FOR RUBBER HYDROCHLORIDE AND THE FIBRE IDENTITY PERIOD

At a temperature of 90° C. or higher, rubber hydrochloride becomes elastic and rubbery and can be racked in a manner similar to rubber[26]. Elasticity sets in at a temperature lower than that at which the crystalline diagram is appreciably affected but, undoubtedly, the elasticity is associated with a weakening of the lattice forces due to thermal agitation. Of course, even at room temperature, films of rubber hydrochloride can be elongated 400 or 500% if the stretching is done slowly and carefully, but the recovery from such elongations is poor. The elasticity of rubber hydrochloride should be of interest for theories of elasticity because of the absence of unsaturation and the marked dependence on temperature. However, some unsaturation may still exist because rubber hydrochloride can undergo a type of vulcanization[27].

Figures 19 and 20 give curves showing the racking phenomena. Racked at 90° C., rubber hydrochloride does not have a sharp "melting-point" but when racked at 115° C., the temperature at which it begins to retract is very definite. The tensile strength of a piece of rubber hydrochloride racked to 1000% elongation at 120° C. was about 7000 lbs. per sq. in., based on the final cross section.

Racked samples of rubber hydrochloride give fibre diagrams indicative of crystal orientation. Figure 21 is the diagram of a sample racked to 500% elongation at 95° C. Figure 22 is a pattern for racked petroleum-ether sol rubber, for comparison. Figure 23 is a pattern for racked rubber hydrochloride taken at a long film-specimen distance to investigate large spacings[28]. The purpose was to show more intimately the nature of the central blackening which occurs in the rubber hydrochloride patterns. The intense spots on the meridian, *i. e.*, in the direction of the fibring, just outside of the lead bead, represent a spacing of 82 Å. The

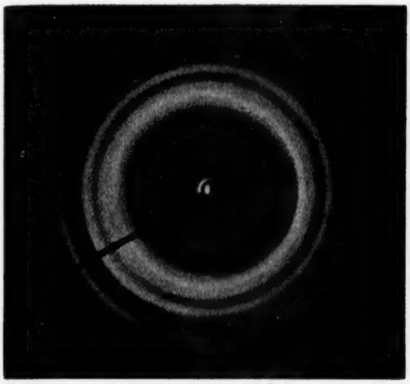

FIG. 7.—Balata. Film-specimen distance 50 mm.

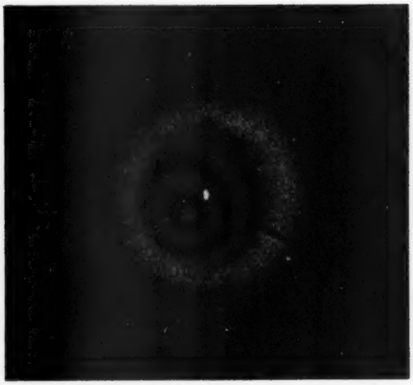

FIG. 8.—Monocyclorubber. Film-specimen distance 50 mm.

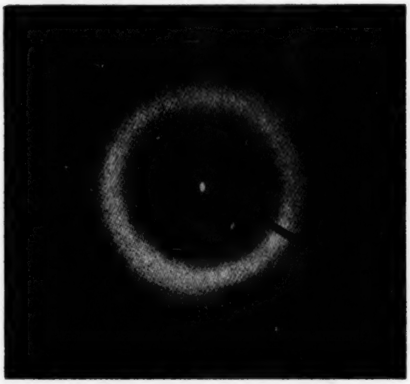

FIG. 9.—Alpha-isorubber. Film-specimen distance 50 mm.

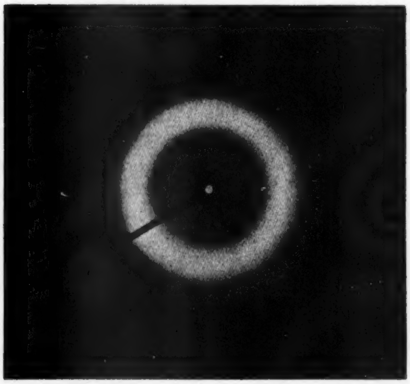

FIG. 10.—Polycyclorubber. Cyclizing agent: Boron trifluoride. Film-specimen distance 50 mm.

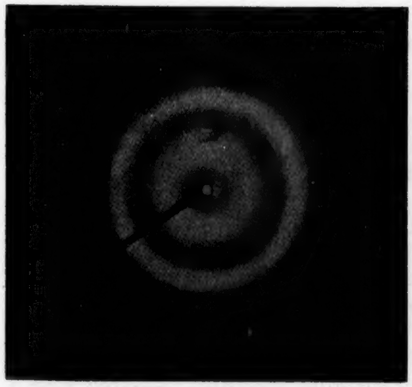

FIG. 11.—Balata hydrochloride, 30.8% chlorine. Film-specimen distance 50 mm.

FIG. 12.—Rubber hydrochloride. Temperature 105° C. Film-specimen distance 50 mm.

next spacing on the meridian "spokes" figures out to be 16 Å. These spacings represent periodicities along the fibre axis, the former one approaching colloidal dimensions. It will be seen later that 82 Å is approximately nine times the dimension of the unit cell along the fibre axis (the value 82 Å is not so very accurate since the calculated spacing is extremely sensitive to the diameter for such large spacings), and so represents a periodicity in structure for every 18 or 20 repeating chemical groups along the long chain molecules. About one out of ten groups, as determined by the chlorine content, has not added hydrogen chloride.

To determine the periodicity along the fibre axis and the lattice spacings, accurate measurement of the specimen-film distance is required. This was accomplished by taking two pictures at different film distances without disturbing the

TABLE II

X-RAY DIFFRACTION DATA FOR RACKED RUBBER HYDROCHLORIDE, CuKα RADIATION, $\lambda = 1.54$ Å

Spot	θ degrees	$d = \frac{\lambda}{2 \sin \theta}$ Å	Relative intensity $D = \log_{10} \frac{I \text{ background}}{I \text{ spot}}$
A_1	7° 25′	5.96	.3
A_2	8° 32′	5.19	1.0
A_3	15°	2.98	.2
A_4	16° 9′	2.77	.1
A_5	19°	2.36	.06
A_6	20° 8′	2.24	—
I_1	9° 43′	4.56	1.4
I_2	12° 24′	3.59	.3
I_3	16° 28′	2.72	.02
II_0	9° 38′	4.60	1.3
II_1	13° 11′	3.38	.3
II_2	18° 42′	2.40	.01
II_3	20° 8′	2.24	.01
II_4	21° 39′	2.09	.01
III_1	15° 56′	2.81	.02
III_2	17° 13′	2.60	.01
III_3	18° 54′	2.38	.01
IV_0	21° 33′	2.10	.01

specimen. The distance the film holder was moved between exposures was measured with a suitably mounted travelling microscope. The films were measured with a low-power travelling microscope. From the distance which the film holder was moved and the measurements of the two films, the specimen-film distance for the exposures could be accurately determined. The films used in this way for measurements of the lattice spacings are reproduced in Figures 24 and 25. Two independent determinations were made.

The results of the measurements are given in Table II. Equatorial spots are designated by the letter A and a subscript numbering the spots from the centre of the diagram. Thus A_2 is the second spot from the centre, on the equator. Similarly, the Roman numerals refer to the layer lines and the spots are numbered from the meridian, *i. e.*, II_3 is the third spot from the meridian on the second layer line.

The relative intensities given are the photographic densities measured with a Zeiss spectrum line photometer.

THE CRYSTAL STRUCTURE OF RUBBER HYDROCHLORIDE

In view of the uncertainty and controversy which exists, after 13 years, over the interpretation of the x-ray diagram of rubber[29, 30, 31] despite the accuracy of the measurements[32], the first attempt at an explanation of the diagram of rubber hydrochloride should perhaps be regarded as no more than tentative, a starting point from which the argument can proceed. Nevertheless, it is considered to be worth while to report a proposed interpretation of the diagram. It should be recognized that such a solution is not unique and that other solutions may exist which will give as satisfactory agreement with the data. The final solution must give, in addition to a prediction of the lattice spacings, an explanation of the intensity relations. In order to determine the crystal structure, it is very advantageous to have highly oriented preparations, so that three x-ray diagrams may be taken with the beam traversing the three crystal axes. Such specimens have not yet been secured with rubber hydrochloride but it is extremely probable that eventually a way will be found to obtain them. Meantime, the following interpretation is offered for the data.

The period along the fibre axis was determined as 9.1 Å. This should be accurate to ±0.1 Å. For the other two dimensions of the unit cell it can be assumed that the equatorial spots A_1 and A_2 represent planes (200) and (002), respectively, in an orthorhombic lattice. Hence, the other two dimensions of the unit cell are twice the lattice spacings of these spots or $a=11.92$ Å and $c=10.38$ Å. The equatorial spot A_1 is especially interesting because of its low intensity compared to A_2 and the strong intensity of its second order. A_1 coincides with the K_β satellite of A_2 and so cannot be recognized unless the K_β radiation is eliminated. Using these dimensions for the unit cell, $a=11.92$ Å, $b=9.10$ Å, $c=10.38$ Å, observed values of $\sin^2\theta$, should satisfy the equation

$$\sin^2 \theta = 0.004165\ h^2 + 0.007156\ k^2 + 0.005503\ l^2$$

Observed and calculated values of $\sin^2\theta$ are given in Table III, together with proposed indices for the spots. In several cases, where there is some uncertainty, two sets of indices are given. Agreement of observed and calculated values is good for all the more intense spots.

To calculate the number of hydrochlorinated isopentene groups in the unit cell, there is the formula:

$$z = \frac{V \times d}{M \times 1.65}$$

Here z is the number of groups, V is the volume of the unit cell in Å^3, d is the density in g. per cc. and M is the molecular weight of the repeating group. The volume of the unit cell is 1126 Å^3. The density of rubber hydrochloride was determined to be 1.147. Racked to 1000% elongation it was 1.193. The molecular weight of the group is 104.5. Substituting these values gives $z=7.8$.

Assuming that z is 8 and calculating d, this gives the x-ray density as 1.226. The value of z is probably within the experimental error of being equal to 8. A possible reason for a low experimental value of d, as compared to the x-ray value, is that the chlorine content is lower than theoretical.

Having determined the crystal system and the unit cell dimensions, it remains to fix the positions of the eight repeating groups in the cell and to determine the space group. Speculations in this respect will not be carried very far here. Four long chain molecules, extending in the direction of the fibre axis, and each supplying two repeating groups should undoubtedly be regarded as making up the unit cell.

TABLE III

TEST OF THE PROPOSED CRYSTAL STRUCTURE

Spot	Indices (h, k, l)	$\sin^2\theta$ observed	$\sin^2\theta$ calculated
A_1	200	.0167	.0167
A_2	002	.0220	.0220
A_3	400	.0670	.0666
A_4	401	.0773	.0721
A_5	{500, 501}	.1060	{.1041, .1096}
A_6	403	.1184	.1162
I_1	012	.0285	.0292
I_2	212	.0461	.0458
I_3	411	.0804	.0793
II_0	020	.0280	.0286
II_1	022	.0520	.0506
II_2	421	.1028	.1008
II_3	422	.1185	.1173
II_4	{520, 423}	.1361	{.1327, .1447}
III_1	031	.0754	.0699
III_2	032	.0876	.0864
III_3	{033, 330}	.1049	{.1139, .1019}
IV_0	040	.1349	.1145

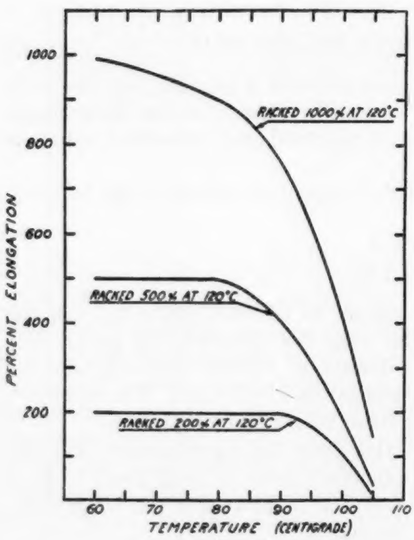

FIG. 19.

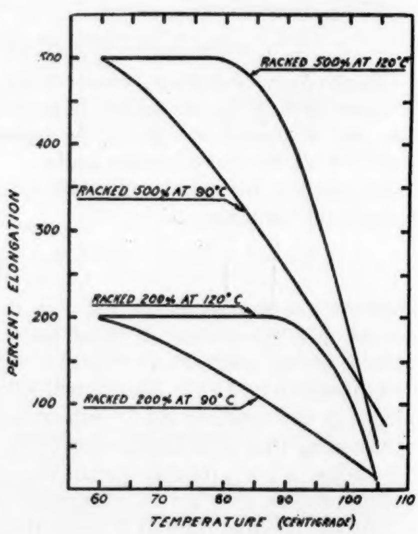

FIG. 20.

FIG. 13.—Rubber hydrochloride. Temperature 115° C. Film-specimen distance 50 mm.

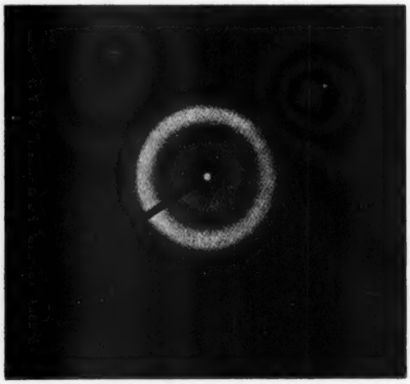

FIG. 14.—Rubber hydrochloride. Sample of Figure 13 recrystallized. Room temperature. Film-specimen distance 34 mm.

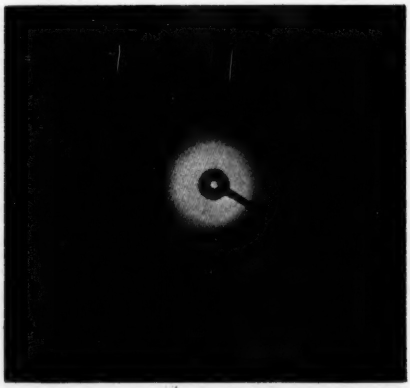

FIG. 15.—Rubber hydrochloride and solvent. 40% by volume acetylene tetrachloride, Film-specimen distance 35 mm.

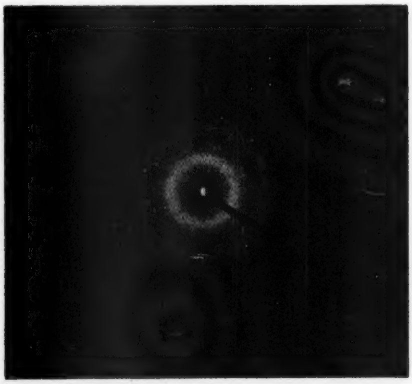

FIG. 16.—Rubber hydrochloride and solvent. 25% by volume acetylene tetrachloride. Film-specimen distance 35 mm.

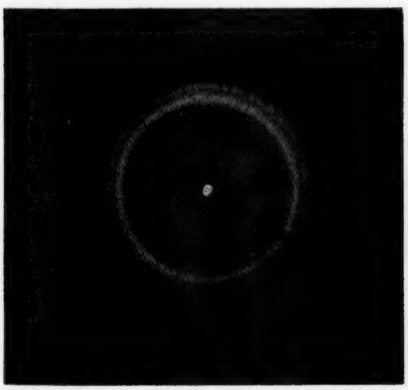

FIG. 17.—Rubber hydrochloride and plasticizer. 15% by volume dibutyl phthalate. Temperature 110° C. Film-specimen distance 50 mm.

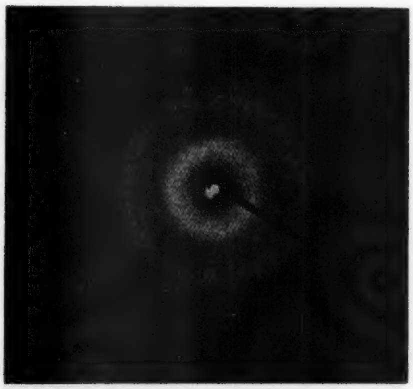

FIG. 18.—Rubber hydrochloride and plasticizer. Sample of Figure 17. Temperature 115° C. Film-specimen distance 50 mm.

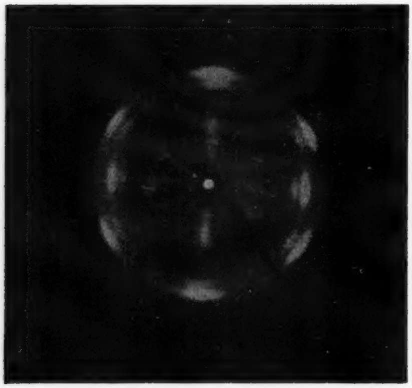

FIG. 21.—Racked rubber hydrochloride. 500% elongation. Film-specimen distance 50 mm.

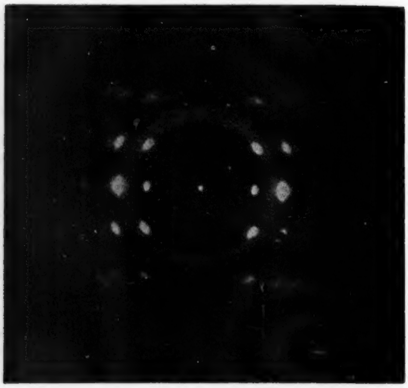

FIG. 22.—Racked sol rubber. 1000% elongation. Film-specimen distance 35 mm. Exposure 5 hours.

FIG. 23.—Racked rubber hydrochloride—large spacings. 1000% elongation. Film-specimen distance 100 mm. Exposure 20 hours.

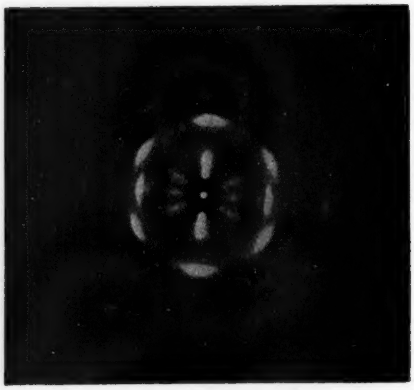

FIG. 24.—Racked rubber hydrochloride. 1000% elongation. Film-specimen distance 34.4 mm. Nickel filter. Exposure 7 hours.

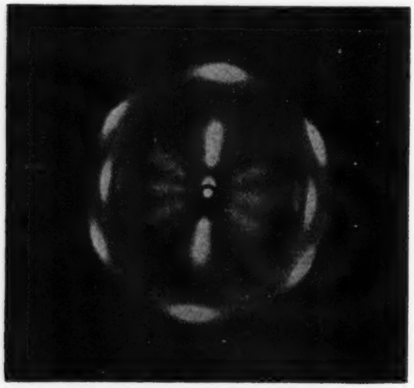

FIG. 25.—Racked rubber hydrochloride—Same specimen as Figure 24. Film-specimen distance 55.4 mm. Nickel filter. Exposure 8 hours.

A difficulty at once arises. Assuming a carbon-carbon distance of 1.54 Å, a valence angle[11] of 109° 28′ and the zig-zag paraffin chain, the length of two groups is 10.0 Å as compared to the fibre axis period of 9.1 Å. Even by shading the values to 1.5 Å and 109°, as was done to get the balata groups to fit in the cell[33], the length is 9.76 Å. A similar difficulty was experienced by Fuller and Erickson[34] in explaining the fibre period of linear polyesters, which led them to assume that the chains were distorted into "tub" forms. Sauter[30] has also considered the possibility that the normal zig-zag paraffin chain can be distorted into a "tub" form by thermal agitation or by other atoms. In view of this accumulating evidence, it is justifiable to assume that the chlorine atoms have caused the rubber hydrochloride chain molecules to take on a shorter form than the planar, zig-zag normal paraffin chain. It does not appear profitable to draw pictures of possible chain shapes without more definite information about the exact nature of the distortion. As regards the symmetry arrangements of the chains to give the observed intensities, the general principles used by Sauter[30] in explaining the rubber diagram should apply. The possibility also exists that stereoisomeric right and left hand chains occur, giving a crystal which is essentially a molecular racemate. The amorphous structure of balata hydrochloride may be due to an isomeric difference in the chains resulting from the original *trans* form of balata and the *cis* form of rubber.

CONCLUSIONS

The x-ray diagram of rubber hydrochloride is a worthy addition to those of other natural high polymers and derivatives, and its study is a fruitful field for investigating the internal structure of such materials.

Various peculiarities have been pointed out which have raised a question as to whether the properties of rubber hydrochloride can be explained on the basis of a chemical structure consisting of long, chlorinated, paraffin chains. These disturbing facts are (1) the effect on the x-ray diagram of the first addition of hydrogen chloride; (2) the failure to secure the theoretical chlorine content; (3) the possibility of vulcanization; (4) the amorphous diagram of balata hydrochloride, and (5) the shortening of the chains compared to normal paraffin chains.

A partial departure from the strict formula may, in turn, lead to a colloidal structure which may be essential for such properties as the elasticity shown at higher temperatures and the ability to rack.

The interpretation of the x-ray diagram seems to be possible on the basis of such long chains if some deformation from the zig-zag form is permitted to shorten them about 10%.

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THE OXIDATION PRODUCTS OF RUBBER *

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1. INTRODUCTORY

In their summary of the aging of vulcanized rubber, Porritt and Scott[1] state that three factors are responsible for the changes in mechanical properties of vulcanized rubber during aging, viz.: (*a*) oxidation of the rubber; (*b*) after-vulcanization; (*c*) some colloidal change of the rubber, sometimes termed aggregation.

Of these factors, oxidation is by far the most important because it is responsible for the decrease in mechanical properties, which leads to the general deterioration of rubber from a technical standpoint. It was Marzetti[2] who proved that the decrease of mechanical properties in accelerated aging is due to oxidation. Later, Kohman[3] confirmed this in a more concise way and showed that even such small amounts as 0.5% of oxygen absorbed by vulcanized rubber are sufficient to decrease tensile properties to 50% of their original value.

When studying aging, three ways of tackling this problem are possible, *viz.:*

(1) Investigations of the mechanical properties, either under normal conditions, or under special conditions such as elevated temperature or high speed.

(2) Determination of oxidation products, which are formed during oxidation of the rubber.

(3) Direct determination of the amount of oxygen which is absorbed by the rubber.

It is clear that any of these methods may be combined with accelerated aging tests.

It is our intention to limit ourselves in this treatise to the second method, *i.e.*, the determination of oxidation products. Various older investigations have been carried out in this direction, but mostly with rubbers which were oxidized so far that they had no more interest from a technical standpoint[4]. The authors were especially interested to isolate oxidation products from technical vulcanized rubber products in a preliminary stage of oxidation where the exterior of the rubber did not show any deterioration and even the mechanical properties had not decreased to a considerable extent. It is obvious that from a technical standpoint it is of great importance to be able to predict, in this initial stage of oxidation, whether a vulcanized rubber article will age well.

In 1929 the authors[5] published a method which allowed them to determine oxidation products in vulcanized rubber. Since then the Netherlands Government Rubber Institute has made a routine trial of this method, applying it in many aging problems, where other methods would have failed to give an insight in this difficult domain. On the other hand, it seems that this method has not acquired the general attention which, in our opinion, it deserves. In various handbooks which have appeared since 1929 it has either not been mentioned at all, or only superficially. For that reason it seemed timely to give a review of the

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method at the symposium on durability, as it has been improved since 1929. Moreover, opportunity is taken to give a number of examples, showing the importance of this method in giving an insight into the aging of vulcanized rubber.

2. IMPROVED TECHNIQUE OF ISOLATION OF OXIDATION PRODUCTS

During the ten years which have elapsed since our previous communication, the technique of isolation of the oxidation products has been improved considerably.

The method now in use may be described as follows:

Determination of Alcoholic Potash Extract.

Five grams of the vulcanized rubber are first extracted with acetone for 8 hours and dried for 15 minutes at 60° C. To this acetone-extracted rubber are added 50 cc. of benzene, and the rubber is swollen for one night (16 to 18 hours) in the dark. After adding 50 cc. of alcoholic potash (0.5 N) the liquid is boiled for 4 hours under a reflux condenser. The liquid is poured off and filtered if necessary. The rubber is thoroughly washed twice with portions of 50 cc. boiling alcohol (96%) and once with hot distilled water. The combined filtrate and washings are evaporated nearly to dryness (3 to 5 cc.), taken up in 50 cc. distilled water, and after adding 10 cc. 25% hydrochloric acid, transferred to a separating funnel and extracted 3 times with 40 cc. pure ether. The combined ethereal extract is washed 2 to 3 times thoroughly with distilled water and subsequently allowed to stand for 30 minutes over anhydrous sodium sulfate. The dried ether solution is filtered into a tared Berntrop-flask, the ether distilled, and the extract dried at 105° C. to constant weight. The residue is termed the alcoholic potash residue.

Determination of Oxidation Products.

To the alcoholic potash residue, 15 cc. alcoholic potash (0.5 N) are added and the liquid is heated for 1 hour on a water-bath under a reflux condenser. The liquid is decanted carefully and the flask rinsed with water, taking care that no deposits are swept away by the water.

The residue, in the form of skins, usually adheres to the bottom of the flask. After adding a small quantity of water the residue is loosened by shaking. If the residue sticks persistently to the glass, the flask is heated on the water-bath until the residue is loosened. These oxidation products are filtered over asbestos in a Gooch crucible, washed with water and subsequently once with alcohol, and dried at 105° C. The residue is termed oxidation-products.

From the analytical standpoint a few questions may be pointed out which are of importance in respect of the results of this procedure:

(*a*) Originally benzene was chosen as a swelling liquid, but the question arose later whether other swelling liquids for rubber could also be used with success for this determination. In consequence, vulcanized rubbers of increasing degrees of vulcanization were subjected to the determination of oxidation products with the aid of various swelling liquids, *viz.*, ether, petrol (100 to 130° C.), benzene and chloroform, the swelling being lowest for ether and highest for chloroform. The results have been collected in Table I.

As is seen, the amount of oxidation products obtained with ether, petrol and chloroform is in all cases lower than with benzene. In consequence, benzene may be supposed to be the most suitable liquid for this purpose.

(*b*) It should be pointed out that the ether, which is used for extraction of the alcoholic potash extract of the swollen rubber, should be entirely free of peroxides[6]. Commercial ether often contains a considerable amount of peroxides, and the amount of oxidation products determined was shown to be less in the case of the use of ether containing peroxides, *e. g.*, in one case with pure ether, 2.3% oxidation products were found against 1.8% with ether containing peroxides. Distillation of the ethereal liquid should take place the same day, to prevent the formation of peroxides or oxidation products present in any other form.

(*c*) If bituminous compounds are present in the rubber, these would be found in the alcoholic potash extract and be determined as oxidation products. In that case the rubber after acetone extraction is subsequently extracted by chloroform to eliminate the bitumen. This is only to be considered as a partial solution of the difficulty, as after chloroform extraction, the amount of oxidation products present is found to be too low.

Table I

Determination of Oxidation Products with Various Swelling Liquids

	Vulcanization coefficient			
	1.6	3.6	4.9	6.2
Ether.	%	%	%	%
Alcoholic potash extract	0.3	0.4	0.5	0.6
Oxidation products	0.04	0.02	0.04	0.1
Petrol (100°–130° C.).				
Alcoholic potash extract	0.4	0.5	0.6	1.0
Oxidation products	0.1	0.1	0.2	0.4
Benzene.				
Alcoholic potash extract	0.5	0.7	0.8	1.0
Oxidation products	0.2	0.3	0.4	0.6
Chloroform.				
Alcoholic potash extract	0.4	0.5	0.4	0.6
Oxidation products	0.3	0.3	0.3	0.3

3. FORMATION OF OXIDATION PRODUCTS DURING VULCANIZATION AND AGING

In our first communication on this subject, we have given examples of the formation of oxidation products during vulcanization and during aging of simple rubber-sulfur mixings. We may now show a few figures for more technical mixings (see Table II) with various organic accelerators.

Mixings were made and vulcanized as stated in Table II. The vulcanizates were subjected to an accelerated aging test in the Geer oven during 7×24 hours at 70° C. Both vulcanizates and the aged samples were subjected to analysis and the amount of oxidation product determined by the method just described.

The results of these analyses have been compiled in Table III. As is distinctly seen, there is a formation of oxidation products during vulcanization and an increase during aging at 70 C. In the mixing with D. P. G., the amount of oxidation products increases with increasing time of vulcanization, and the increase during aging is also largest. The amounts of oxidation products in the vulcanizates with Captax and Tuads are smaller, which is in full agreement with the knowledge of the aging quantities of such mixings. The amount of oxidation products in the benzoyl peroxide vulcanizate is much larger, which is also in agreement with the bad aging of this mixing.

It is clear that the increase in oxidation products during aging is caused by a direct oxidation owing to the oxygen absorbed from the air. On the other hand the formation of oxidation products during vulcanization in absence of direct contact with oxygen requires further consideration.

TABLE II

COMPOSITION OF THE MIXINGS

Mixing	A	B	C	D
First latex crepe	100	100	100	90
Sulfur	3	2.5	2.5	—
Zinc oxide	3	5	3	—
D. P. G.	1	—	—	—
Captax	—	0.75	—	—
Tuads	—	—	0.5	—
Stearic acid	—	1	1	—
Dibenzoyl peroxide	—	—	—	10
Temperature of vulcanization	147° C.	130° C.	130° C.	147° C.
Time of vulcanization (min.)	15–60	10–60	10–60	15–60

TABLE III

FORMATION OF OXIDATION PRODUCTS DURING VULCANIZATION AND AGING OF MIXINGS A, B, C, AND D

	%	%	%	%
Mixing A with D. P. G., vulcanized for	*15*	*30*	*45*	*60 min.*
Acetone extract	5.5	4.0	3.2	2.8
Oxidation products	0.1	0.2	0.3	0.4
After 7 × 24 hrs. at 70° C.				
Acetone extract	5.4	3.7	3.0	2.8
Oxidation products	0.2	0.4	0.6	0.9
Mixing B with Captax, vulcanized for	*20*	*30*	*40*	*60 min.*
Acetone extract	6.7	5.4	4.7	4.1
Oxidation products	0.1	0.1	0.1	0.1
After 7 × 24 hrs. at 70° C.				
Acetone extract	4.0	3.7	3.7	3.5
Oxidation products	0.3	0.3	0.3	0.3
Mixing C with Tuads, vulcanized for	*20*	*30*	*40*	*60 min.*
Acetone extract	4.4	3.8	3.7	3.6
Oxidation products	0.1	0.1	0.2	0.2
After 7 × 24 hrs. at 70° C.				
Acetone extract	3.4	3.3	3.4	3.4
Oxidation products	0.4	0.3	0.4	0.4
Mixing D with dibenzoyl peroxide, vulcanized for	—	*10*	*30*	*60 min.*
Acetone extract	—	6.8	6.6	6.8
Oxidation products	—	0.6	0.6	0.6

It was shown formerly that the oxidation products contain 3 to 5% (average 4%) of oxygen. If 1% of oxidation products is present this amounts to 0.04% of oxygen, or for 100 grams of rubber to about 40 milligrams. In the case of small amounts of oxidation products, the oxygen may have originated from the air, which is dissolved in all rubber, but for larger amounts of oxidation products this explanation would not suffice.

In 1931 Cotton[7] showed that the mastication process is partly an oxidation process, confirmed in an entirely different way by Busse[8]. In this relation there seemed a possibility that oxidation products in vulcanized rubber were developed

during masticating. To confirm this suggestion we carried out the following masticating experiments.

F. L. crepe was masticated on the mixing mill

(a) for normal time (5 min.);
(b) much longer than normal (30 min.);
(c) for 30 min. with continuous cutting and cooling in air.

These masticated rubbers were mixed with sulfur and vulcanized at 147° C. for increasing times. The amounts of oxidation products found in these vulcanizates have been compiled in Table IV.

It is obvious from these figures that the amount of oxidation products is not influenced by the method and time of masticating, and therefore the suggestion that oxidation products develop during mastication must be rejected.

TABLE IV

INFLUENCE OF MASTICATING ON THE AMOUNT OF OXIDATION PRODUCTS

Mixing: F. L. Crepe........... 92.5 parts
Sulfur .... 7.5 "

Vulcanized at 147° C. during	1 hr.	3 hrs.	4 hrs.
Normally masticated 5 *min.*	%	%	%
Acetone extract	8.9	5.4	4.2
Oxidation products	0.1	0.2	0.3
Masticated 30 *min.*			
Acetone extract	8.8	5.3	4.1
Oxidation products	0.1	0.3	0.3
Masticated 30 *min.* (*as a thin sheet, aired*)			
Acetone extract	8.9	5.4	4.1
Oxidation products	0.1	0.3	0.3

There is left only one possibility, *i. e.*, that the oxidation products are developed during vulcanization either from free oxygen present in the rubber or bound in some labile form, *e. g.*, as peroxides, which may have been formed as pointed out by Busse.

However, the formation of oxidation products is not restricted to vulcanization of rubber with sulfur. As was already shown, vulcanization with dibenzoyl peroxide gives a vulcanizate which contains a relatively large amount of oxidation products.

We have further investigated the oxidation of raw rubber under the influence of light in the presence of a catalyst, and found in this case also that considerable amounts of oxidation products were formed. Pieces of F. L. crepe were soaked in 1% solutions of copper sulfate and ferric acetate, rinsed with water, and exposed in daylight for 7 and 14 days before a window. After these periods analyses were carried out, the results being compiled in Table V.

As is shown distinctly by the data, a considerable amount of oxidation products is formed when raw rubber is oxidized under the influence of light. However, in this case the acetone extract increases at the same time and not, as in the case of vulcanized rubber, in a later stage of oxidation. The results of these experiments show therefore that the determination of oxidation products in the rubber is a more sensitive method for detecting oxidation than the simpler determination of the acetone extract.

TABLE V

OXIDATION PRODUCTS IN RAW RUBBER

	Control in dark	Seven days in light	Fourteen days in light
F. L. crepe	%	%	%
Acetone extract	2.9	2.9	4.0
Alcoholic potash extract	0.4	0.7	2.8
Oxidation products	0.01	0.2	1.8
F. L. crepe dipped in CuSo₄ (1% *solution*)			
Acetone extract	2.9	3.2	14.3
Alcoholic potash extract	0.4	1.0	12.8
Oxidation products	0.06	0.6	9.6
F. L. crepe, dipped in Fe acetate (1% *solution*)			
Acetone extract	2.9	3.7	10.6
Alcoholic potash extract	0.5	1.2	7.7
Oxidation products	0.06	0.6	6.3

4. APPLICATIONS OF THE DETERMINATION OF THE OXIDATION PRODUCTS IN TESTING RUBBER ARTICLES

In the course of years the determination of oxidation products has been applied in many cases of testing work and has proved a most useful instrument in predicting the aging of vulcanized rubbers.

We may consider a few cases:

(*a*) If the amount of oxidation products in the rubber article to be tested is already high, we may be sure that the article will show rapid aging, the amount of oxidation products increasing considerably.

(*b*) If the article shows a low figure for oxidation products, this does not make it certain that it will show slow aging. It is advisable to carry out accelerated aging tests and to determine the amount of oxidation products after the aging tests. If, after these tests, the data for oxidation products are high, this will show insufficient aging resistance, but if the figure is low, this shows good aging quality.

When testing rubber articles which allow the determination of mechanical properties, *e. g.*, tensile properties, aging may usually be tested by the change in mechanical properties before and after accelerated aging tests, and there is no immediate necessity to determine oxidation products. However, in some cases, such data may be a useful addition in judging the results of aging, especially if the article under consideration has to show very good aging qualities.

If, however, the rubber article cannot be tested by mechanical tests, the determination of the oxidation products, before and after aging, provides a most useful test, no other method being available. This is the case, for example, with such articles as mouth-pieces of gas masks, corrugated hose, proofed goods, such as hospital sheet and single texture for camera shutters.

We wish to give a few examples of the results of this kind of testing work. From a number of corrugated hose (for gas masks) the oxidation products were determined before and after aging tests during 7×24 hours at 70° C. (Geer-Evans) and during 2×24 hours at 60° C. and 20 atm. of oxygen (Bierer-Davis). The results have been compiled in Table VI, and also the condition of these hose after 2 years has been given in this table.

The hose tested have been arranged in three groups. In group A we find the hose containing before the aging tests a considerable amount of oxidation products, which increases under the influence of the aging tests; their condition was bad after 2 years of natural aging. Group B shows a small amount of oxidation

product, but after aging this has increased considerably; their condition was fair after 2 years. The last group shows a small percentage of oxidation products and a small increase after aging. The condition of these hose was excellent after 2 years. From the experience of a large amount of testing work of rubber parts

TABLE VI

OXIDATION PRODUCTS IN SAMPLES OF CORRUGATED HOSE

Group	Control	After 7 × 24 h. at 70° C. (Geer-oven test)	After 2 × 24 h. (Bierer-Davis bomb test)	After 2 years
	%	%	%	
A	0.2	0.9	H(a)	Bad
	0.2	1.3	H(a)	"
	0.1	0.9	3.4	"
	0.3	1.0	4.5	"
B	0.1	0.4	4.2	Medium
	0.2	0.7	3.1	"
	0.2	0.5	4.5	"
C	0.1	0.2	1.3	Good
	0.1	0.1	0.6	"
	0.1	0.1	0.6	"
	0.2	0.1	0.6	"
	0.1	0.1	1.0	"

(a) Hard after Bierer-Davis aging test.

TABLE VII

OXIDATION PRODUCTS IN RUBBER PARTS OF GAS MASKS BEFORE AND AFTER THE GEER TESTS

Group A			Group B		
Control	After 7 × 24 hrs. 70° C. (Geer test)	Condition after natural aging for 5 years	Control	After 7 × 24 hrs. 70° C. (Geer test)	Condition after natural aging for 5 years
%	%		%	%	
0.1	0.3	g	0.3	1.0	d
0.2	0.3	g	0.4	1.0	d
0.2	0.5	g	0.2	0.9	d
0.1	0.4	g	0.2	1.3	d
0.1	0.5	g	0.4	1.1	g
0.2	0.5	m	0.1	0.8	g
0.1	0.1	g	0.2	0.7	g
0.4	0.6	g	0.2	1.5	d
0.1	0.1	g	0.3	0.8	m
0.1	0.2	g	0.3	0.8	m
0.2	0.2	g	0.1	0.9	m
0.2	0.4	d	0.1	0.8	d
0.1	0.3	g	0.1	0.7	m
0.1	0.1	g	0.1	0.8	d
0.1	0.2	g	0.2	0.7	d
0.1	0.5	g	0.1	1.2	m

After 5 years: g = good. m = medium. d = deteriorated.

of gas masks, the Netherlands Government Rubber Institute has developed a specification which states that the amount of oxidation products before aging shall not exceed 0.4%, and after aging in the Geer-oven during 7×24 hours at 70° C. this amount shall not be more than 0.6%. For 7 years this has been the basis of tests on rubber parts of gas masks, which cannot be tested by tensile tests. That this basis has proved reliable may be shown from the data in Table VII.

In this Table the data for oxidation products before and after the Geer-test for a number of rubber parts have been compiled, and also their outward (exterior) condition after 5 years of normal aging (in boxes, temperature not exceeding 20° C.).

In group A we see rubber parts, which all comply with the specifications, and after 5 years of normal aging their condition is good, with the exception of two, one being bad, the other fair.

In group B we see a number of rubber parts, which have been tested and which agree with the specification before the aging test. However, after the Geer-test the amount of oxidation product has increased above the limit of 0.6% which is allowed. After 5 years most of these have deteriorated, a number are fair, and only three are supposed to be good according to their outward condition.

From these figures it is obvious that the determination of oxidation products before and after accelerated aging is considered to be of utmost importance for the testing of rubber parts of gas masks. Similar testing routine has been developed for hospital sheet and for single texture for camera shutters. For this material it is specified that the amount of oxidation products before the Geer test should not exceed 0.4%, and after that test 0.8%. This has given considerable satisfaction in practice.

5. OXIDATION PRODUCTS IN COMPARISON WITH PYRROLE FIGURES

In the foregoing paragraphs we have given data to prove the importance of the determination of the oxidation products in judging the initial stages of oxidation of vulcanized rubber. However, it cannot be denied that the method is somewhat tedious and can be applied with success only by experienced personnel. A more easy test, detecting the initial stage of oxidation of vulcanized rubber, would therefore be most welcome.

In 1930 Temple, Cadwell and Mead, published a new test, which may be termed the quantitative pyrrole test. It is known from Gorter[10] that oxidized raw rubber shows the socalled pyrrole test, but this was only a qualitative phenomenon, probably caused by levulinic aldehyde present in oxidized rubber.

The American investigators succeeded in developing this reaction into a quantitative test. The rubber is cut into thin slices, the sample heated with ammonium acetate, water added and the liquid subsequently distilled. The distillate is shaken twice with a small quantity of ether, and this ethereal extract added to an alcoholic pine wood extract with alcoholic hydrochloric acid. The color obtained is compared with standard colors made previously. This method, which is rather easy to carry out, was applied with a few analytical alterations to oxidation phenomena of vulcanized rubber. A simple rubber-sulfur mixing was vulcanized for increasing times. The vulcanizates were subjected to various accelerated aging tests, and the oxidation products as well as the pyrrole figures were determined before and after the various aging tests.

The results have been compiled in Table VIII. If we consider the figures before the aging tests, we see that the pyrrole test does not give any indication in respect of oxidation but, on the other hand, the oxidation products show figures which indicate that the over-vulcanized rubber is already oxidized. In this respect the oxidation products are to be preferred to the pyrrole figure.

After aging in the Geer oven, the figures for oxidation products and pyrrole more or less run parallel. After the Bierer-Davis test, high pyrrole figures are obtained. For this reason Bierer-Davis aging tests under varied conditions of temperature and time were carried out and the pyrrole figures determined. The results have been collected in Table IX.

From these figures it is obvious that during the Bierer-Davis test at 60° C. the pyrrole figures increase considerably, even such a high figure as 300 being obtained. This seems to be caused by the combined effect of oxygen and temperature, because the increase at 20° C. and 40° C. is only small.

TABLE VIII

OXIDATION PRODUCTS AND PYRROLE FIGURES

Mixing: F. L. Crepe .... 92.5 parts
Sulfur .... 7.5 "

Vulcanized at 147° C. during	1 hr.	2 hrs.	3 hrs.	4 hrs.
After vulcanization (without aging)				
Combined sulfur	1.0%	2.3%	4.0%	5.5%
Oxidation products	Trace	0.1%	0.3%	0.4%
Pyrrole figures	—	—	—	—
After 7 × 24 *hrs. at* 70° C.				
Oxidation products	Trace	0.3%	0.6%	0.8%
Pyrrole figures	—	0.1	0.2	0.2
After 14 × 24 *hrs.* at 70° C.				
Oxidation products	0.2%	0.8%	2.2%	2.6%
Pyrrole figures	0.4	0.6	0.8	1.0
After 2 × 24 *hrs. Bierer-Davis* 60° C.				
Oxidation products	0.1%	0.3%	1.0%	2.5% + 17.0% *a*
Pyrrole figures	1.8	8.0	17.0	80.0

(*a*) Oxidation products insoluble in ether.

TABLE IX

PYRROLE FIGURES AFTER AGING TESTS

Mixing: F. L. Crepe .... 100 parts
Sulfur .... 5 "
D.P.G. .... 1 "
Zinc oxide .... 3 "

Vulcanized at 147° C. during	10 min.	30 min.	50 min.
Control (not aged)	0	0	0
Geer test			
After 7 × 24 hrs. at 70° C.	Trace	1.1	2.8
Bierer-Davis test (20 *atm. oxygen*)			
After 2 × 24 hrs. at 60° C.	15	140	300
" 3 × 24 " 60° C.	25	300	300
" 3 × 24 " 20° C.	0	1.0	2.0
" 3 × 24 " 40° C.	Trace	4.0	5.2

Further investigation should establish the origin of these exceptionally high pyrrole figures at 60° C. From these results we may conclude that for testing work the determination of oxidation products is to be preferred to the pyrrole test. However, from a scientific standpoint, the pyrrole test certainly deserves further investigation.

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[6] Peroxides in ether may be eliminated by shaking with a 5% solution of ferrous sulfate in 2.5% hydrochloric acid. For 1 liter of ether use 100 cc. of this solution and shake for a few minutes. The ether is controlled in the following way. In 5 cc. of water a few crystals of ferrous sulfate are dissolved, and a few drops of hydrochloric acid are added. The liquid is shaken in a test tube with 10 cc. of ether. After addition of ammonium thiocyanate, the water layer must show only a faint rose color. For the determination of the alcoholic potash extract, this purified ether is kept in a brown flask above a layer of ferrous sulfate solution and is shaken before use.

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MECHANISM OF OXIDATION OF RUBBER AND ITS BEARING ON ACCELERATED AGING TESTS *

PARTS I AND II

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PART I

It is now generally recognized that the aging of rubber is a chemical process involving oxidation of the rubber. This process must possess definite chemical reaction constants, and the ideal method of foretelling what will happen to a sample of rubber when submitted to various specified oxidizing conditions is to measure these constants. Unfortunately vulcanized rubber is a complicated system, and it is likely that the unravelling and measurement of these constants will be correspondingly complicated.

There is, however, a distinct possibility that an examination of the process of rubber oxidation under different conditions of temperature and oxygen pressure will yield information which will be of practical value, not only from the point of view of helping to assess what is the most that can be expected from accelerated aging tests, but also by indicating what further technical effects are possible and whether the limit has been reached by empirical methods in the protection of rubber against oxidation.

Despite the bulky literature on the perishing of rubber there is very little quantitative data on the effect of varying temperature, oxygen pressure, and incident light on the rate of oxidation.

Kohman[1] oxidized sheets of vulcanized rubber at 80° C. in oxygen maintained at constant pressure. Over the complete oxidation range of the rubber he obtained autocatalytic type curves relating the oxygen consumption with time. He also confirmed the observation of Marzetti[2] that only 1% of oxygen is required to destroy all rubber properties. Kohman was more concerned with the effect of variation in the internal factors such as degree of vulcanization and antioxidant addition rather than with the external factors, oxygen pressure and temperature.

Williams and Neal[3], using a much simpler technique and limiting themselves to the first one per cent. of the oxidation, which is the region of direct interest to the rubber technologist, showed that the rate of oxidation was independent of the pressure of oxygen providing the oxygen was able to diffuse rapidly through the rubber. This was shown to be so for a rubber-sulfur vulcanizate and an unvulcanized rubber containing copper. If the rubber was in the form of sheets, that is, the rubber-oxygen interface was small, the rate of oxidation was then dependent on the rate at which oxygen could diffuse into the rubber, and the rate of oxidation observed varied with the pressure of oxygen.

They interpreted this zero order reaction effect as being due to a slow transfor-

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mation of the rubber to an oxidizable form, this being oxidized as quickly as it is formed. The scheme of their suggested mechanism may be represented thus:

Rubber $\rightarrow$ Rubber A (slow) 1
Rubber A + O_2 $\rightarrow$ Rubber O_2 (fast) 2

This is not very attractive, as it is difficult to understand for example how antioxidants which normally function by destroying peroxides can retard the first rate-determining process.

In any case the zero order of the oxidation with respect to oxygen does not necessarily mean that there is a specific rate-determining reaction not involving oxygen, but rather that the kinetic consequences of the mechanism yield a formula for the rate of the oxidation in which the concentration of oxygen does not appear. Our own view is that the autoöxidation of rubber has a similar mechanism to that suggested for other autoöxidations, *viz.*, a chain mechanism.

A. FACTORS IN THE OXIDATION OF RUBBER

1. The Effect of Temperature.

(a) The Temperature Coefficient of the Oxidation of Rubber.

It is readily seen that if the relative propensities for two rubbers to age at room temperatures are estimated by measurements made at an elevated temperature, a serious error is introduced if they have different temperature coefficients of oxidation.

The determination of the rate at which the oxidation of rubber is increased by increasing temperature is important not only for this reason, but is also the first step towards unravelling the mechanism of the reaction. If the mechanism is such as to result in the rate of reaction being proportional either to the velocity constant of a slow rate-determining reaction or to a number of different reaction constants or their reciprocals multiplied together, then the zero order rate of oxidation should conform with the well-known Arrhenius equation:

$$\log_e \text{rate} = A - \frac{Q}{RT}$$

This point can readily be tested, because Williams and Neal have given measurements on the effect of temperature.

In order to employ their data for this purpose it is necessary to relate the decrease in pressure $\left(\frac{dp}{dt}\right)$ in which their measurements are expressed with the rate of oxygen consumption $\left(\frac{dx}{dt}\right)$. The total oxygen in their apparatus, ignoring the quantity in the capillary tube, is given by:

$$x = \frac{1}{22400} \cdot \frac{p}{760} \left\{ \left(v - \frac{n}{\rho} \right) \frac{273}{T} + 0.0001456 n e^{4040/RT} \right\} \text{mols.}$$

where p = pressure of oxygen in mm. of mercury,
v = volume of bulb in cc.,
n = no. of grams of rubber,
T = temperature in °A.,
and ρ = density of rubber.

The quantity $0.0001456ne^{4040/RT}$ represents the amount of oxygen dissolved in the rubber in N.T.P. cc., and has been calculated from the data given by Williams and Neal for the solubility of oxygen in rubber at 0°, 12° and 29° C.

The rate of disappearance of oxygen in terms of moles of oxygen per unit time per gram of rubber is therefore given by:

$$\frac{dx}{dt}=\frac{dp}{dt}\frac{1}{n(22400)(760)}\left\{\left(v-\frac{n}{\rho}\right)\frac{273}{T}+0.0001456ne^{4040/RT}\right\}$$

If n is small this approximates to:

$$\frac{dx}{dt}=\frac{dp}{dt}\frac{v'273}{n(22400)(760)}\cdot\frac{1}{T}$$

where v' is the volume of the gas space $=v-\frac{n}{\rho}$. The Williams and Neal data between 26° and 80° C. conforms with the equation:

$$\log_{10}\frac{dp}{dt}\cdot\frac{1}{T}=6.467-\frac{10,290}{2.303RT}$$

The comparison of the observed rates and those calculated from the above equation is shown in Table I.

TABLE I

THE EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION OF AN UNACCELERATED VULCANIZATE

	Rate of oxygen consumption $\frac{dp}{dt}$ (mm. Hg. per hr.)	
Temperature	Williams and Neal	Calculated
26° C.	26	25.9
42° C.	75	65.3
56° C.	138	139.0
70° C.	280	274.2
80° C.	428	427.6
90° C.	604	665.3
100° C.	750	981.8

The deviations at 90° and 100° C. may be due to the high temperature effects discussed later.

The value of Q is 10,290 calories and the value of A when the rate of oxidation is expressed in moles of oxygen per gram of rubber per second is 2.890.

The rubber employed by Williams and Neal for obtaining the measurements used above was a mixture of 100 parts of smoked sheet and 10 parts of sulfur vulcanized for 5 hours at 140° C. and acetone-extracted.

The importance of the evaluation of these constants for rubbers containing various amounts of combined sulfur, in the presence of antioxidants, needs no stressing. Some preliminary measurements were made to ascertain whether the different rates of oxidation obtained by changing these factors were due to alterations in the value of A or Q or both. A mix was chosen that would give a combined sulfur content different from that employed by Williams and Neal, and measurements were made with and without antioxidant. The mix employed was rubber 100, sulfur 3, zinc oxide 5, diphenylguanidine 1.5. This was cured in sheets about 1 mm. thick for 90 minutes at 141° C. The sheets were cut into strips, acetone-extracted and the acetone removed by evacuation.

It was uncertain at the outset which would be the best method of measuring the rate of oxidation, and the composite apparatus illustrated (Fig. 1) was erected. It

consists of a constant pressure apparatus in which the pressure is automatically controlled as the oxidation proceeds. This portion of the apparatus is similar to that employed and fully described by Kohman[1]. In addition, the apparatus provides facilities whereby the bulb containing the oxidizing rubber can be isolated from the constant pressure device, and rates of oxidation can be measured either with a simple mercury manometer or, if the rate of oxidation is slow, with a Warburg manometer.

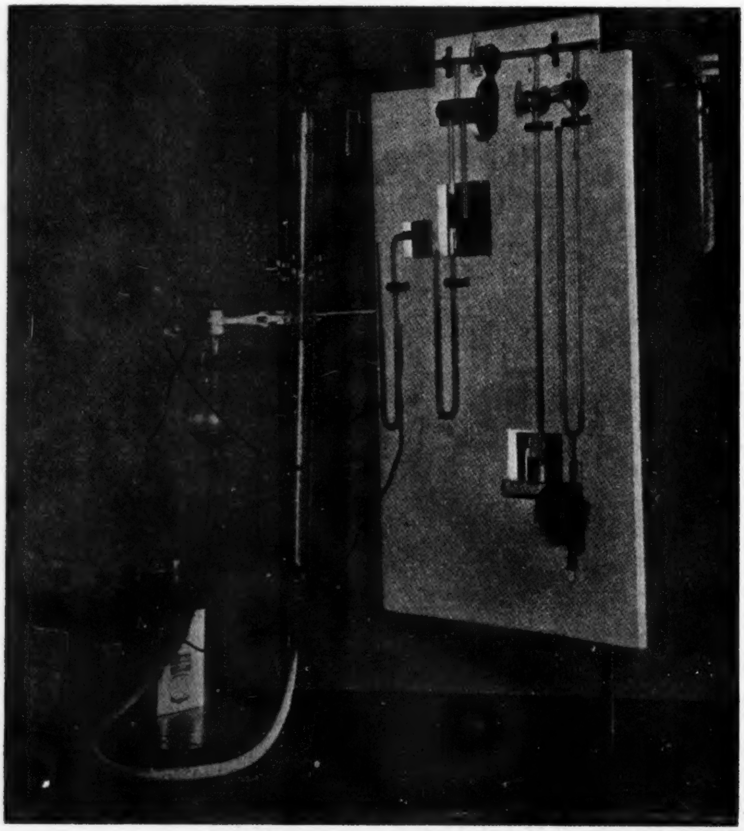


FIG. 1.—Apparatus for measuring rate of oxidation of rubber.

It was found that the rate of oxidation over a small range of the oxidation could be more accurately measured with the manometer than with the constant pressure device, and the major portion of the data given here was obtained with the mercury manometer.

When several measurements were made on the same sample of rubber, further measured supplies of oxygen could be readily introduced into the bulb, and the amount of oxygen consumption over the complete series of measurements was automatically registered.

Five grams of the acetone-extracted rubber were introduced into the bulb of the apparatus and the rate of oxidation was then measured at temperatures between

36° and 66° C. At each temperature the rate at which mercury climbed the manometer was noted until a steady rate was attained. The bulb was then raised to the next temperature and the process repeated.

Measurements were made in a precisely similar manner on a portion of the rubber into which dimethoxydiphenylamine had been introduced by allowing the sample to stand in a 1% acetone solution of the antioxidant for several days immediately after acetone extraction. The results are tabulated below and the plots of $\log_{10} \frac{dp}{dt} \cdot \frac{1}{T}$ against $\frac{1}{T}$ are shown in Figure 2. The data conform with the Arrhenius equation in that a straight line plot is obtained. It will be seen in Table II that the observed values and those calculated from $\log_{10}\frac{dp}{dt} \cdot \frac{1}{T} = 1390 - \frac{5180}{T}$ for the unprotected vulcanizate, and $\log_{10}\frac{dp}{dt} \cdot \frac{1}{T} = 8.62 - \frac{3657}{T}$ for the vulcanizate containing dimethoxydiphenylamine are in fair agreement.

TABLE II

THE EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION OF A DIPHENYLGUANIDINE VULCANIZATE WITH AND WITHOUT ANTIOXIDANT

Temperature (° C.)	Unprotected vulcanizate: $\frac{dp}{dt}$ observed (mm. Hg. per hr.)	Unprotected vulcanizate: $\frac{dp}{dt}$ calculated (mm. Hg. per hr.)	Vulcanizate containing dimethoxydiphenylamine: $\frac{dp}{dt}$ observed (mm. Hg. per hr.)	Vulcanizate containing dimethoxydiphenylamine: $\frac{dp}{dt}$ calculated (mm. Hg. per hr.)
36.00	0.59	0.422	—	—
40.60	0.86	0.726	—	—
44.60	1.20	1.119	0.38	0.400
48.95	1.82	1.832	0.56	0.546
54.65	4.095	3.954	0.95	0.940
61.10	7.65	8.204	—	—
64.05	—	—	2.00	1.963
65.83	13.65	13.65	2.22	2.227

These data indicate that for the vulcanizate containing no antioxidant the value of Q is 23,620 calories and the value of A is 6.378 (when rates of oxidation are expressed as moles oxygen per gram of rubber per sec.). The corresponding figures for the vulcanizate containing dimethoxydiphenylamine are:

$$Q = 16{,}670 \text{ calories and } A = 1.098.$$

Measurements were not made above 66° C. for the sample in sheet form, as it was expected that at higher temperatures the dimensions of the sample would become the governing factor. The experiment was repeated with the difference that the vulcanized sheets were shredded between cold rolls before acetone extraction. The rates of oxidation were measured at temperatures between 85° C. and 59° C., commencing at the higher temperature and introducing further supplies of oxygen into the bulb as required. The rates observed are given in Figure 3. The dotted curve corresponds to the equation $\log_{10}\frac{dp}{dt} \cdot \frac{1}{T} = 14.337 - \frac{5205}{T}$, indicating a value for Q of 23,730 calories and A of 6.738.

Measurements were made also at temperatures near 120° C. on another sample of the same vulcanizate. The rate of decrease in pressure was about 1000 mm. of mercury per hour, whereas the figure calculated from the equation found to hold up to 80° C. indicated a theoretical rate of 4910 mm.

(*b*) *Theoretical.*

These effects of varying oxygen pressure and temperature are not inconsistent with the hypothesis that the autoöxidation involves a reaction between the rubber double bonds and a peroxide. The simplest interpretation is that we have the following mechanism:

$$B + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} BO_2 \text{ (fast)}$$

$$BO_2 + R \xrightarrow{k_3} RO_2 + B.$$

Here R represents a rubber double bond and B some substance capable of forming a peroxide with atmospheric oxygen.

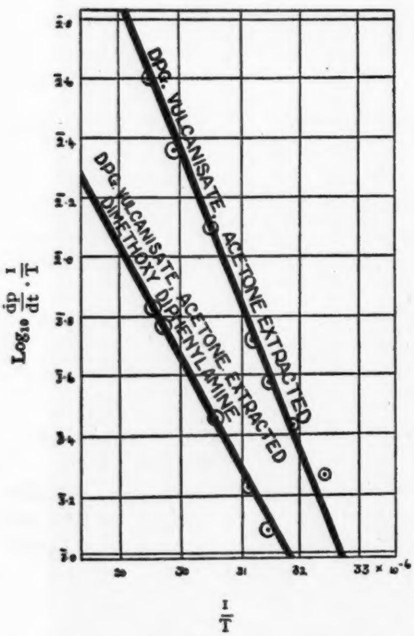


Fig. 2.

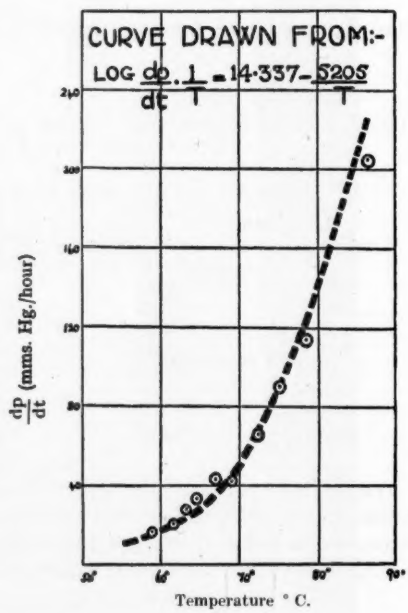


Fig. 3.

If k_2 is much smaller than k_1, that is the rate of decomposition of the peroxide BO_2 is much slower than the rate of peroxide formation, then the rate of oxidation is given by $k_3[R]\beta$, where β is the concentration of the substance B in the rubber. For small oxidation ranges over which the concentration of the rubber double bonds does not vary appreciably, this may be written $k_3'\beta$.

This simple hypothesis adequately explains the fact that the oxidation is of zero order with respect to oxygen and also that the rate varies according to the Arrhenius equation, but it becomes rather strained when we attempt to explain the variations observed in the constants A and Q with different vulcanizates.

It is far more likely that the autoöxidation of rubber is similar to the autoöxida-

tion of other substances, that is, it involves a chain mechanism. On this basis the simplest scheme required to explain the data so far available is the following:

$$R \underset{k_5}{\overset{k_4}{\rightleftharpoons}} R^* \qquad \ldots\ldots\ldots\ldots \quad 1$$

$$R^* + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RO_2^* \qquad \ldots\ldots\ldots\ldots \quad 2$$

$$RO_2^* + R \xrightarrow{k_3} RO_2 + R^* \qquad \ldots\ldots\ldots\ldots \quad 3$$

$$RO_2^* \xrightarrow{k_6} RO_2 \qquad \ldots\ldots\ldots\ldots \quad 4$$

Here R^* is an activated rubber double bond, RO_2^* is a rubber peroxide and RO_2 represents the consequence of rubber oxidation.

Process 1 represents the thermal activation of double bonds and a possible degradation to the normal state. Process 2 represents the equilibrium involving the activated double bond, oxygen and the peroxide. These two processes constitute the chain initiation part of the mechanism.

The rubber peroxide will collide frequently with the double bonds in its immediate vicinity due to thermal agitation of the polymer chains. It is imagined that one of the collisions results in a degradation of the peroxide to an oxidized rubber double bond and the simultaneous activation of the rubber double bond with which the fruitful collision took place. This activated double bond then forms a peroxide with oxygen according to reaction 2, and the process repeats itself. Thus a number of successive neighboring double bonds are activated, combine with oxygen to form a peroxide, and degenerate into an oxidized double bond. This reaction path proceeds through adjacent double bonds in the rubber structure, not of necessity in the same rubber molecule, until the chain ending mechanism occurs (process 4). In the absence of antioxidant this is presumed to be a degeneration of the peroxide without the attendant transfer of energy to an adjacent double bond.

After a period of time the number of reaction chains in the rubber and the rate of oxidation attain a steady equilibrium value. This equilibrium is reached when the number of chains ending in unit time becomes equal to the number of chains beginning. Under these equilibrium conditions $\frac{d[R^*]}{dt}$ and $\frac{d[RO_2^*]}{dt}$ are zero. If the reaction path or reaction chain length is long, the rate of oxidation is given by $k_3[RO_2^*][R]$.

If $\qquad [RO_2^*] = \beta, \quad [R^*] = \alpha, \quad [R] = r,$

and the concentration of oxygen in the rubber is p', since

$$\frac{d\alpha}{dt} = 0,$$

then the rate of formation of R^* = rate of disappearance of R^*, or

$$k_4 f(r) + k_3 \beta f(r) = k_5 \alpha + k_1 \alpha p'.$$

Similarly since $\qquad \frac{d\beta}{dt} = 0,$

the rate of formation of RO_2^* = rate of disappearance of RO_2^*,

$$i.\ e., \quad k_1 \alpha p' = k_2 \beta + k_3 f(r) + k_6 \beta.$$

As at the most the oxidation of the first 1% of the rubber only is in question, the value of r is practically unchanged and may be regarded as constant. Let $k_3f(r)=k_3'$ and $k_4f(r)=k_4'$. Elimination of α from these equations gives:

$$\beta=\frac{k_1k_4'p'}{k_1p'(k_2+k_6)+k_5(k_2+k_3'+k_6)}$$

The rate of oxidation is then:

$$k_3'\beta=\frac{k_1k_3'k_4'p'}{k_3p'(k_2+k_6)+k_5(k_2+k_3'+k_6)}.$$

If k_5 and k_2 are small, *i. e.*, in the chain initiation portion of the mechanism the reversion of the peroxide to form oxygen and a normal rubber double bond is unlikely, then the rate of the oxidation is given simply by:

$$-\frac{d[O_2]}{dt}=\frac{k_3'k_4'}{k_6}=\frac{k_3''k_4''}{k_6'}e^{-(Q_3+Q_4-Q_6)/RT}$$

or
$$\log_e\frac{d[O_2]}{dt}=\log_e\frac{k_3''k_4''}{k_6'}-\frac{Q_3+Q_4-Q_6}{RT}$$

Thus the rate of oxidation is independent of the oxygen pressure and obeys the equation

$$\log_e\frac{d[O_2]}{dt}=A-\frac{Q}{RT}$$

In the presence of an antioxidant an additional chain-breaking mechanism is introduced between the rubber peroxide and an antioxidant molecule, and the existence of a fifth process may be postulated:

$$RO_2^*+i\xrightarrow{k_7}\text{deactivated products} \qquad \ldots\ldots\ldots\ldots \quad 5$$

where i is an antioxidant.

If this is now the preponderating chain breaking mechanism process 4 may be ignored and the rate of the oxidation is given by $\frac{k_3'k_4'}{k_7f[i]}$. The decrease in the constant A observed on addition of antioxidant is then due to the temperature-independent part of the product $k_7f[i]$ being larger than that of k_6, and the decrease in the value of Q due to Q_7 being larger than Q_6.

(*c*) *The Deviation from the Theoretical Rate at High Temperatures.*

Above 80° C. there is a rapidly increasing deviation, with increasing temperature, of the observed rate of oxidation from the rate anticipated from the measurements made at lower temperatures. The temperature coefficient of the reaction falls rapidly above 80° C. It has been shown also by Williams and Neal that at high temperatures the rate of oxidation of rubber varies with the pressure of the oxygen.

Thus it appears that the oxidation of rubber at temperatures below and above 80° C. has different characteristics.

Below 80° C. the rate of oxidation is independent of the pressure and varies with temperature according to the Arrhenius equation. Above 80° C. the rate of oxidation falls with decreasing oxygen pressure, and the rate of oxidation at about 1 atmosphere pressure increases only relatively slowly with temperature. This deviation is of great interest and warrants a close inspection of two possible explanations. These are:

A. Permeation of oxygen at high temperatures is not sufficiently fast to enable oxygen to reach the interior of the rubber sample.

B. The assumptions made concerning the relative values of the reaction constants in the postulated mechanism of the autoöxidation are not true for temperatures above 80° C. Both these possibilities are considered in detail below.

Below a critical temperature, depending on the dimensions of the sample, the rubber has dissolved oxygen throughout its mass, and every portion of the rubber is undergoing slow oxidation. Above this critical temperature the rate of chemical union of oxygen with the rubber is so fast that oxygen is unable to diffuse throughout the mass of the rubber. Consequently above this critical temperature only the outside layers of the rubber sample are being oxidized and a lower rate of oxidation is observed than that expected.

The possibilities of this non-homogeneous oxidation occurring was recognized by Kohman, and for his measurements he chose a dimension for his oxidizing samples that ensured a large rubber/air interface. The importance of this factor in accelerated aging tests was also stressed by Daynes[4] and by Williams and Neal.

From the preceding formula showing the effect of temperature and oxygen pressure on the rate of oxidation it is possible to estimate the order of magnitude of the equilibrium or maximum depth of oxygen penetration and to show approximately how it varies under different conditions. It may therefore be assessed whether it will become an important factor in Geer oven aging, particularly at higher temperatures, and whether this is the only reason for the deviation from the Arrhenius equation above 80° C.

To do this several simplifying assumptions are made. The rate of oxidation of rubber was shown by Williams and Neal to be independent of oxygen pressure down to a low pressure. It can therefore be assumed, without introducing a large error, that the rate of oxidation of the rubber is independent of the concentration of oxygen to the point where all the oxygen is consumed. Daynes has pointed out that the permeability of rubber to oxygen decreases at first with oxidation and then increases, presumably due to cracking of the oxidized rubber. It is assumed that the permeability remains constant.

When equilibrium conditions have been attained in the sheet of oxidizing rubber, suppose that at a depth of x cm. from the surface the concentration gradient is c, and at a depth $x+\delta x$ it is $\dot{c}+\delta\dot{c}$. The quantity of oxygen passing through 1 square cm. of the plane parallel with the surface at depth x per sec. will be equal to the sum of the quantity passing through 1 sq. cm. of the plane at depth $x+\delta x$ per sec. and the quantity of oxygen combining with δx cc. of rubber per second. If K is the diffusivity constant, k is the rate of oxidation, and ρ the density of the rubber, then

$$K\dot{c}=K(\dot{c}+\delta\dot{c}+\delta x\rho k$$

$$\text{or}\qquad \frac{d\dot{c}}{dx}=\frac{d^2c}{dx^2}=-\frac{\rho k}{K}$$

$$\text{and}\qquad c=-\frac{\rho k}{2K}x^2+lx+l'.$$

The integration constants l and l' are removed by considering the conditions at the surface of the rubber. When $x=0$,

$\frac{dc}{dx}=0$, and $c=$ the solubility of oxygen in the rubber at the pressure of oxygen p at the surface of the sheet,

$=Ap$ where A is the solubility at 1 atmosphere.

$$\therefore\ c=-\frac{\rho k}{2K}x^2+Ap.$$

The depth of penetration d is obtained when the concentration c is O, *i. e.*, when

$$x=d=\sqrt{\frac{2AKp}{\rho k}}$$

The product AK is equal to the permeability coefficient P.

$$\therefore\ d=\sqrt{\frac{2Pp}{\rho k}}$$

An approximate estimation of the variation of permeability of oxygen through rubber with temperature can be obtained from the literature. Daynes states that the temperature coefficient of oxygen permeability for rubber is 6.3% for each 1° C. between 15° and 25° C. From data given by Edwards and Pickering[5] the specific permeability for oxygen at 25° C is 1.5×10^{-7} N.T.P. cc. per sec. per sq. cm. per cm.

The specific permeability at a temperature T° abs. can therefore be represented by $P_T=0.2117e^{-8340/RT}$ N.T.P. cc. per sec. per sq. cm. per cm.

The rate of oxidation of one sample of rubber was shown to vary with temperature according to the equation $\log_{10}$ (rate of oxidation of molecules O_2 per sec. per g. of rubber)

$$=6.378-\frac{23,620}{2.303RT}$$

or rate of oxidation$=5.35\times10^{10}e^{-23620/RT}$ N.T.P. cc. per sec. per g. of rubber. On introducing these values of k and P into the expression for depth of penetration and assuming $p=1$ atmosphere and $\rho=0.92$, then $d=2.933\times10^{-6}e^{7640/RT}$. The values of d calculated from this for various temperatures are:

25° C.	1.230 cm.
50° C.	0.452 cm.
75° C.	0.191 cm.
100° C.	0.091 cm.

It must be remembered that these figures are based on oxidation rates measured on one sample of rubber and permeability measurements made on another and can be taken only as being very approximate.

To assess in a qualitative manner the validity of the expression, blocks of rubber were placed in the Geer oven at 70° C. and 100° C., and transverse sections were examined from time to time. The blocks had the dimensions $1\frac{1}{2}\times1\frac{3}{4}\times2$ inches, and were made from a diphenylguanidine gum mix with and without an antioxidant. The depth of discoloration varied little with increasing time in the oven, and was for the samples not containing antioxidant about 1 mm. at 100° C. and 4 mm. at 70° C. The block containing antioxidant showed a depth of 6 mm. at 70° C. It will be seen from the above equation that the rate of oxidation, k, occurs in the denominator, so that decrease in k will lead to an increase in d, accounting for the increased penetration in the presence of an antioxidant. There is thus a qualitative agreement in the order of magnitude of the calculated and observed depth of penetration, and the latter varies in the direction predicted by the theoretical expression on increasing the temperatures and on reducing the rate of oxidation of the rubber by adding antioxidant.

It can be expected from these figures that nonhomogeneous oxidation will occur in test pieces of normal dimensions in the Geer oven at high temperatures, particularly if the rubber has a high oxidation rate.

It is not likely, however, that the deviation observed at 85° C. with the shredded vulcanizate (Fig. 3) is due to this, for the following reasons. In sheet form a similar rubber obeyed the Arrhenius equation up to 66° C. and possibly higher (Fig. 2) yet increasing the surface area of the rubber many times and reducing the distance of the innermost section of the rubber from the surface at least tenfold results in a deviation from the Arrhenius expression at a temperature only 20° C. higher. Increasing the temperature a matter of 20° C. would decrease the depth of penetration under the most favorable conditions only by a factor of 3 or 4.

It is therefore probable that between 80° C. and 90° C. the decomposition of the rubber peroxide by heat becomes appreciable and k_2 and/or k_5 can no longer be ignored.

(2) THE EFFECT OF IMPURITIES IN THE RUBBER.

(*a*) *Variability in the Oxidation Rate of Unextracted Rubber.*

It is possible that the impurities in non-acetone-extracted vulcanizates may modify the mechanism of the oxidation or may superimpose another type of oxidation, *e. g.*, a catalyzed one, on the chain mechanism suggested above. The anti-

TABLE III

VARIATION IN THE RATE OF OXIDATION OF UNTREATED CRUMBED VULCANIZED RUBBER WITH OXYGEN CONSUMPTION

N.T.P. cc. of oxygen combined per 10 grams of rubber	$\frac{dp}{dt}$ (mm. Hg per hr.)
0	8.35
9.4	7.30
17.3	6.52
28.1	6.46
53.6	5.60

oxidant activity of the acetone-soluble impurities in rubber has long been recognized[6,7], and Dufraisse and Drisch[8] have made a careful examination of their effect on the oxidation rate. They examined also the effect of what may be termed the artificial impurities, *viz.*, free sulfur and accelerators, and concluded that they had little effect. From this it would appear that the oxidation mechanism of non-acetone-extracted vulcanizates should be very similar to that of the acetone-extracted; the only difference being the presence of a natural antioxidant which would function according to reaction 5.

Measurements made on the shredded diphenylguanidine vulcanizates before acetone extraction soon showed that the impurities played an important role in the oxidation mechanism, quite apart from any changes they may have induced in the rate of oxidation. An attempt was made to measure the temperature coefficient. The first oxidation gave a gradually decreasing rate of oxidation with decreasing pressure of oxygen but subsequent measurements gave steady rates. These rates did not conform with the Arrhenius equation. On plotting $\log_{10} \frac{dp}{dt} \cdot \frac{1}{T}$ against $\frac{1}{T}$, a straight line could not be drawn through the points.

An examination of the data showed that the rubber was apparently decreasing in its propensity for oxidation with each succeeding measurement. Several measurements were made at 70° C. on the same mix. After the rate had been determined the sample was allowed to oxidize at the same temperature and the measurement repeated from time to time, oxygen being introduced into the apparatus as required. The rate of oxidation gradually decreased (Table III).

(b) Effect of Evacuation at 100° C. on the Rate of Oxidation:

This drift in the oxidation rate was surprising because Kohman has shown quite the opposite effect when examining the course of oxidation of a vulcanized sheet of rubber at constant pressure over the complete oxidation range. These results were obtained over a small initial portion of the oxidation range where the general Kohman autocatalytic effect was very slight, only 0.76 g. of oxygen per 100 g. of rubber having been consumed when the measurements were discontinued. Furthermore, the samples employed by Kohman were in the form of sheets, whereas the samples employed here were shredded and had also been subjected to varying pressures during the oxidation measurements.

The samples on which these decreasing rates had been observed had been exposed to the diffused light of the laboratory for some time, and it was possible that an excessive amount of peroxide had accumulated.

TABLE IV

THE EFFECT OF EVACUATION AT 100° C. ON THE RATE OF OXIDATION AT 74° C.

Vulcanizate	Treatment	Amount of rubber in apparatus (g.)	Vol. of apparatus (cc.)	Rate of oxidation at 75° C.: $\frac{dp}{dt}$ (mm. Hg. per hr.)	Rate of oxidation at 75° C.: Mols. O_2 per g. of rubber per hr.
Diphenylguanidine vulcanizate containing β-naphthol.	Evacuated at room temperature.	10	65	17.80	4.511
	Evacuated at 100° C. for 30 mins.	10	65	9.65	2.446
Diphenylguanidine vulcanizate containing naphthylamineacetaldehyde condensation product.	Evacuated at room temperature.	9	65	11.46	3.228
	Evacuated at 100° C. for 60 minutes.	9	65	6.55	1.845

If the abnormal initial rates observed are due to this accumulation of peroxide which gradually disappears on oxidation at elevated temperatures, then it is possible that the effect may be overcome by evacuation at high temperatures.

To test this point samples of the shredded untreated vulcanizates showing enhanced initial oxidation rates were heated *in vacuo* at 100° C. in the dark, before making measurements of the rate of oxidation. In each case the rubber was evacuated at 100° C. in the apparatus in which the measurement was to be made. The evacuated bulb was then cooled in ice and filled with oxygen. Similar measurements were made on fresh samples of rubber with the difference that they were evacuated in the usual way at room temperature before filling the apparatus with oxygen. Several measurements were made with different vulcanizates, using different times of evacuation at 100° C. In every case the sample evacuated at 100° C. gave a lower rate of oxidation. Two typical results are given in Table IV.

(c) The Temperature Coefficient of Evacuated Unextracted Vulcanizates.

Even after evacuation at high temperatures difficulty was experienced in taking successive measurements of the rate of oxidation at different temperatures.

The oxidizing rubber appeared to reach its equilibrium value slowly, and the rate observed appeared to depend not only on the temperature of the measurement, but on the immediate prior history of the rubber. It would appear from this that the equilibrium chain conditions were being attained very much more slowly in the case of the unextracted rubbers than in the case of the acetone-extracted samples.

The peroxide concentration varies with temperature according to $e^{-(Q_4-Q_6)RT}$. If the difference between Q_4 and Q_6 is great, raising the temperature of the oxidizing rubber, say 5° C., will result in an appreciable change in the equilibrium peroxide concentration. If this new equilibrium concentration is only attained slowly, an erroneous measurement will be obtained at the higher temperature unless the sample is allowed to oxidize for a sufficient time for the new equilibrium conditions to be reached. Unfortunately this will entail taking measurements on the same rubber for too long a time and over too great a portion of the rubber oxidation range, particularly if measurements are made at several temperatures. This will result in other factors that affect the basic oxidation rate becoming important such as disappearance of antioxidant and the continuation of vulcanization.

The lag in the attainment of equilibrium is very likely the reason for the shape of some of the curves published by Dufraisse and Drisch. Instead of being constant, the rates of oxidation either increase or decrease with time, depending most probably on the immediate prior history of the samples.

The reason for this lag is obscure, and the process is now being investigated in a more suitable form of apparatus.

(3) The Effect of Light.

(*a*) *The Effect of Preëxposure to Light on the Rate of Oxidation.*

It was considered that the peculiar effect of progressively decreasing rates of oxidation observed on the non-extracted crumbed rubber before evacuation (Table III) might have been due to the fact that the samples were exposed for varying lengths of time to the diffused light of the laboratory. It is known that the perishing of rubber is accelerated by light, and it is quite within the realms of possibility that this accelerated rate might persist for some time after removal of the sample into the dark, particularly as there appeared to be a lag in the attainment of peroxide equilibrium.

The following experiment was performed to discover whether this was so or not.

A diphenylguanidine vulcanizate containing 1% of phenyl-β-naphthylamine was spread in crumbed form over a large sheet of glass and a similar sheet of glass supported by a wooden frame placed over it. The rubber was exposed in this way to ordinary daylight in the laboratory. After various times of exposure part of the sample was removed and the rate of oxidation measured at 70° C.

There was a progressive increase in the rate of oxidation in the dark at 70° C. as the time of preëxposure increased (Table V and Fig. 4).

These enhanced rates of oxidation decreased with progressive oxidation in the dark. The results obtained with the samples that had been illuminated for four days and twenty-two days are given in Table VI and illustrated by the dotted curves of Figure 4.

This continuation of the enhanced light oxidation in the dark is possibly the explanation of some of the results reported in the literature on the cracking of the surface layers of vulcanizates in the absence of light (van Rossem and Thalen[9]).

TABLE V

THE EFFECT OF PREËXPOSURE TO LIGHT ON THE RATE OF OXIDATION IN THE DARK AT 70° C.

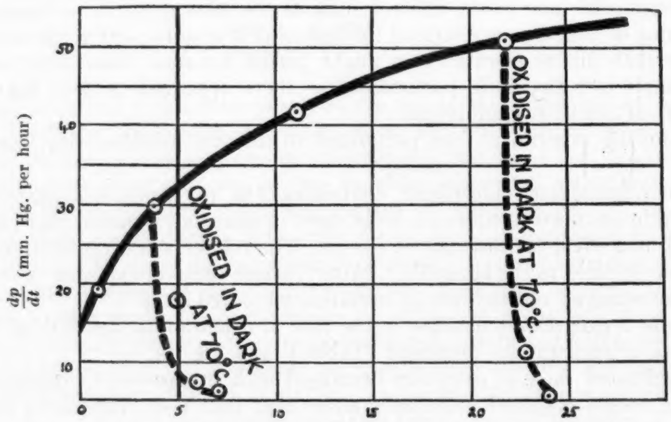
Ten grams of rubber were used in each experiment and the volume of the apparatus employed was 65 cc.

Treatment	Rate of oxidation in the dark at 70° C. $\frac{dp}{dt}$ (mm. Hg. per hr.)
Ex bottle	14.93
Exposed to light for 1 day	18.73
" " " " 4 days	29.33
" " " " 11 "	42.15
" " " " 22 "	51.50

TABLE VI

EFFECT OF PROLONGED DARK OXIDATION AT 70° C. ON THE ENHANCED RATE OF OXIDATION PRODUCED BY PREËXPOSURE TO LIGHT

Treatment	Rate of oxidation at 70° C $\frac{dp}{dt}$ (mm. Hg. per hr.)
Exposed to light for 4 days	29.33
Exposed to light for 4 days and oxidized in dark at 70° C. for 1 day	18.30
2 days	6.90
3 "	5.59
Exposed to light for 22 days	51.50
Exposed to light for 22 days and oxidized in dark at 70° C. for 1 day	11.20
2 days	4.78



Time of preëxposure to light at room temp. (days).

FIG. 4.

Normally, surface cracking is the result of an enhanced surface oxidation due to exposure to light or ozone. If a sample of rubber is inadvertently exposed to light before an examination of its oxidation behavior in the dark it is quite possible that, although there is no evidence of surface oxidation immediately before placing in the dark, the enhanced light oxidation effect will continue and surface cracking will appear apparently without the aid of light.

(*b*) *The Effect of Preëxposure to Light on the Rate of Perishing.*

This effect may be large enough to introduce serious errors into the routine testing of samples of rubber when the samples to be tested are not protected, *e.g.*, by the use of a black pigment, against such an effect. The effect is of course greater with the oxygen bomb than with the Geer oven, since in the former case the activation period may persist throughout the aging period. The effect varies with (*a*) the intensity of the light, and (*b*) the transparency of the compound. In order to show how serious the effect can be, experiments were carried out with a transparent sheet 4 mm. thick (crepe 100, zinc oxide 2, sulfur 3.5, DPG 0.5, vulcanized 70 minutes at 141° C.).

	Tensile strength (kg. per sq. cm.)	Elongation at break (%)
A. Unaged sample stored in dark	152	763
B. Unaged sample exposed 3 hours to winter sunshine in Manchester	155	760
A. Aged for 18 hours in oxygen bomb (70° C. and 300 lbs. per sq. inch)	94	668
B. Aged simultaneously with A	16	350

That the effect is not simply due to an increased degree of vulcanization produced by light is shown by the fact that samples, given an increased heat vulcanization but kept in the dark before testing, did not give a similar drop in tensile strength.

With decreasing transparency the effect became smaller until with compounds colored with gas black the effect could not be detected. Antioxidants, as one would expect, protect even transparent rubbers to a large extent against light activation, for although it is still possible to detect the effect in their presence, it is greatly reduced in magnitude.

The thinness of the samples plays a part also: thus, with sheets 2 mm. thick which were studied by the aid of the bubble blowing machine (Flint and Naunton[10]), it was possible by means of an exposure (to either winter sunlight or to a Quartz U. V. lamp) which had no detectable effect upon tensile properties, to produce sheets which were completely perished in the oxygen bomb in 24 hours when the corresponding unexposed samples still showed (after the same aging) a tensile strength of about 100 kg. per sq. cm.

It is curious that this important effect has been overlooked in drawing up specifications and defining accelerated aging technique. It is not uncommon to see samples awaiting the bomb test spread out on benches directly under windows, with the result that not only would it be impossible to compare the results with those obtained under different conditions, but owing to possible beams of direct sunlight the individual results among themselves might be meaningless. It is certain that a minimum brightness is essential to give the effect; hence while differences between average daylight conditions might not be detected, the difference between an average bright day and a brilliant day will be very marked. It is suggested that in all future official specifications, except perhaps for black goods,

the samples shall be kept in the dark, or at least certainly protected against strong light, before being submitted to an accelerated aging test.

(*c*) *Theoretical.*

Since the rate of oxidation of rubber is proportional to the concentration of peroxide, it would appear that the effect of light is to enhance the peroxide content. The initial rate of oxidation at 70° C. in the dark may be taken as a measure of the peroxide content of the rubber at room temperature immediately before removal from the light, and the effect of light on the peroxide content can be examined in a semi-quantitative manner.

If to the reactions postulated previously is added:

$$R + h\nu \xrightarrow{k_8} R,^*$$

the rate at which rubber double bonds are being activated is given by $k_4' + k_8'f(I)$, where I is the intensity of the incident light and $k_8' = k_8 f(r)$. It was assumed that k_5 and k_2 were small, and thus the rate of formation of peroxide is $k_4' + k_8'f(I)$ and the rate of disappearance of peroxide is $\{k_6 + k_7 f(i)\}\beta$. If at time t the initial rate of oxidation in the dark at 70° C. is x, then since the rate of oxidation

$= k_{3(70°)}\,\beta$, β at time t is $\dfrac{\dot{x}}{k_{3(70°)}}$

$$\therefore \frac{d\beta}{dt} = \frac{1}{k_{3\,(70°)}}\cdot\frac{d\dot{x}}{dt} = k_4' + k_8'f(I) - \{k_6 + k_7 f(i)\}\frac{\dot{x}}{k_{3\,(70°)}}.$$

This gives

$$\dot{x}e^{\{k_6+k_7f(i)\}t} = \frac{k_4' + k_8'f(I)}{k_6 + k_7 f(i)}\,k_{3\,(70°)}\,e^{\{k_6+k_7f(i)\}t} - \left\{\frac{k_4' + k_8'f(I)}{k_6 + k_7 f(i)}\,k_{3\,(70°)} - b\right\}$$

$$\text{or}\quad \dot{x}e^{Et} = De^{Et} - (D - b),$$

$$\text{or}\quad Et = \log_e \frac{D - b}{D - \dot{x}}$$

D is the optimum value of $\dot{x}$ that can be attained by exposure under the experimental conditions employed, and b is the initial rate of oxidation.

The plot of t against $\log_e \dfrac{56.06 - 14.93}{56.06 - \dot{x}}$ is a straight line, showing that the data conform with this equation (Fig. 5). The slope of this line gives 0.1 as the value of E.

The decrease in the rate of oxidation in the dark can be similarly treated, and it can be shown simply that the value of the rate of oxidation $\dot{x}$ at any given time t should be given by the following equation:

$$dt = \log_e \frac{a - Y}{\dot{x} - Y},$$

where a = the initial rate of oxidation,

$$E = k_6 + k_7 f(i),$$

and

$$Y = \frac{k_3' k_4'}{k_6 + k_7 + i}$$

The general trend of the curves showing the decrease in the rate of oxidation in the dark with time are of the same type as those given by the above expression (see dotted curves in Fig. 4).

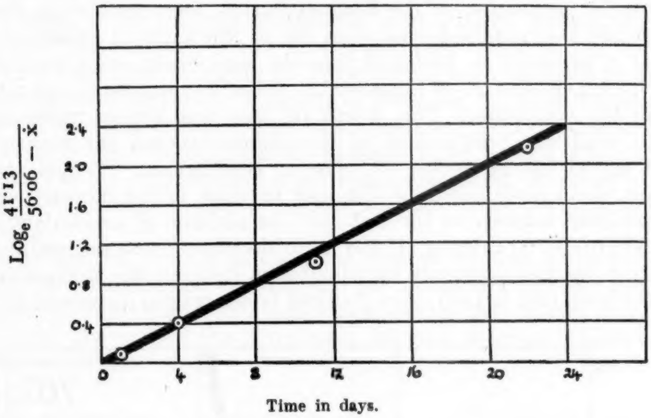


FIG. 5.

PART II

B. THE AUTOCATALYTIC NATURE OF RUBBER OXIDATION

It was on the result of Peachey's experiments on the oxidation of films of raw rubber deposited on the inside of a flask[11] that Ostwald[12] suggested that the oxidation of rubber was autocatalytic. The autocatalytic trend in the oxidation can be observed also in the subsequent measurements of Peachey and Leon[13], Leon and Lister[14] and Kohman. In all these cases the measurements were made over the complete oxidation range, *i.e.*, until the rubber would combine with no more oxygen. It is regrettable that most of the past work on the oxidation of rubber has been based on the complete oxidation of this substance. In the measurements made here over the first small portion of the oxidation range of vulcanized rubber, no evidence of the autocatalytic nature of the oxidation has been observed.

On the chain hypothesis an autocatalytic effect is to be expected, either because the reaction chains develop slowly and take a considerable time to reach their equilibrium value or because some chain-breaking substance present in the system, in this case an antioxidant, is gradually disappearing.

A gradual increase in rate of reaction due to the development of the reaction chains in time can be explained in the following terms. At the outset there are no peroxide molecules in the system. These are gradually formed by the chain initiation reaction at a rate proportional to the amount of autoöxidizing substance present and during the early stages of the oxidation this may be taken to be constant. Therefore peroxide molecules are being formed at a constant rate and are increasing in concentration. At the same time the peroxides are undergoing the chain-propagating reaction, and eventually disappear as a consequence of the chain-ending mechanism. The rate at which peroxides are disappearing is proportional to the concentration of the peroxide, and will therefore be an increasing rate. This increasing rate of peroxide disappearance will eventually become equal to the steady rate of peroxide formation and equilibrium chain conditions will be attained. The gradual increase in peroxide concentration up to the equilibrium value is reflected in an increase in the rate of oxidation and an autocatalytic type of curve will result.

If this is the explanation of the Kohman curves, then equilibrium chain conditions have not been attained even after 700 or 800 hours of oxidation at 80° C. We found it necessary to postulate that the equilibrium chain conditions were attained during the first 20-40 minutes that the rubber sample was in contact with oxygen in the thermostat. This length of time was always necessary for the sample to reach the temperature of the thermostat and the concentration of dissolved oxygen in the rubber to come to equilibrium. The postulation that equilibrium chain conditions were obtained previous to our measurements of the rate of oxidation is based on the fact that the addition of antioxidant reduces Q from 23,600 to 16,700 calories. If the peroxide content was not maintained constant during our measurements by equilibrium between the chain-initiating and ending reactions, then in both cases Q should be the critical increment of the chain-

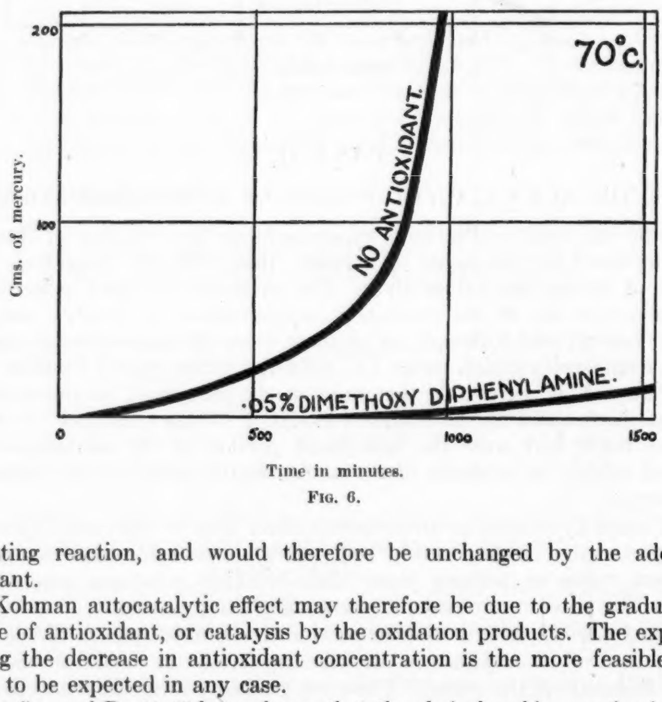


FIG. 6.

propagating reaction, and would therefore be unchanged by the addition of antioxidant.

The Kohman autocatalytic effect may therefore be due to the gradual disappearance of antioxidant, or catalysis by the oxidation products. The explanation involving the decrease in antioxidant concentration is the more feasible, as this effect is to be expected in any case.

Bäckström and Beatty[15] have shown that the chain-breaking mechanism in the case of the autoöxidation of benzaldehyde results in the oxidation of antioxidant, and Stephens[16] maintained that the induction period in autoöxidation is the time necessary for the destruction of inhibitors.

By analogy it is probable that each time an antioxidant molecule deactivates a peroxide in rubber, thus ending a reaction chain, the antioxidant molecule is oxidized. As the rate of oxidation is given by $\frac{k_3'k_4'}{k_6+k_7+(i)}$, there will be an increasing rate of oxidation as reaction proceeds.

This, however, is not the likely explanation of another type of autocatalytic effect met with in rubber oxidation. The curve shown by Dufraisse and Drisch for the early stages of the oxidation of acetone-extracted unvulcanized rubber is

quite different in form from their curves for the oxidation of the vulcanized products. Instead of a rapid rate of oxidation being attained quickly, the tangent of the curve for the oxidation of raw rubber gradually increases from zero.

The effect is illustrated in Figure 6. These curves were obtained by enclosing, in the apparatus used previously, 10 grams of kieselguhr on which 2 grams of acetone-extracted masticated rubber had been deposited from a benzene solution. The autocatalytic effect differs from the Kohman effect in that it is apparent in the early stages of the oxidation and is far more pronounced. It is very likely that this is due not to disappearance of antioxidant but to the development of the chains in time.

This means that the relative values of the rates of reaction of the various portions of the chain mechanism are different for vulcanized and for raw rubber. That progressive vulcanization with sulfur increases the rate of both oxidation and perishing is well known, and this is probably due to a progressive increase in the rate of chain initiation.

C. FACTORS AFFECTING THE EFFICIENCY OF ANTIOXIDANTS AND THEIR RELATIVE EFFECTS UNDER ACCELERATED AND NORMAL AGING CONDITIONS

There is no numerical relationship between oxygen consumption figures and tensile strength deterioration. All that is known is that about 1% of oxygen is required completely to déstroy all rubber properties. This figure may vary with different types of vulcanizates, particularly if they are not at optimum vulcanization. Again there are changes which will take place in rubber and which will affect the tensile properties quite apart from the effect of oxidation, such as continuation of vulcanization and heat deterioration or depolymerization. In comparing two vulcanizates differing only in that one contains an antioxidant, it may be assumed that these effects are very similar in both samples and that the major reason for their different aging behavior resides only in the antioxidant. The effect of an antioxidant which modifies the vulcanization process will not be discussed here, as it involves complicated considerations on the relationship between combined sulfur and physical properties. Apart from this, the fundamental differences in the aging of the two samples will depend on the relative values of the constants A and Q, if light is involved the constants E and D, the dimensions of the samples employed, the rate at which antioxidant may disappear under the specific oxidizing conditions chosen for the comparison, and the mobility of the antioxidant.

1. The Constants A, Q, E, and D.

Although it has not been found possible so far to measure the true relative rates of oxidation at different temperatures for unextracted vulcanizates, it may be assumed that the underlying fundamental oxidation process responsible for the bulk of the aging is that examined in the extracted samples.

The values of A and Q obtained for the four samples of rubber on which measurements are now available are collected together below:

Table I

Vulcanizate	Temp. range (C.)	A	Q calories
Unaccelerated vulcanizate	20–80°	2.890	10,290
Diphenylguanidine vulcanizate	36–66°	6.378	23,620
Diphenylguanidine vulcanizate in shredded form	59–80°	6.738	23,730
Diphenylguanidine vulcanizate + antioxidant	44–85°	1.098	16,670

It will be seen that both A and Q are markedly influenced by the nature of the vulcanizate and by the presence of antioxidants. The large variation in Q which determines the temperature coefficient is disconcerting when it is remembered that the aging properties of rubber are estimated by measurements at a temperature about 30 to 60° C. higher than that encountered under natural aging conditions.

The lower value of Q obtained in the presence of antioxidant means that, as far as homogeneous oxidation of rubber is concerned, the antioxidant will appear more efficient as the temperature is raised. Whether the lowering in Q by an antioxidant is general or not cannot be decided. It depends on the relative values of the critical increments of the reaction between the rubber peroxide and the particular antioxidant employed, *i.e.*, Q_7, and that for the normal chain breaking reaction, *viz.*, Q_6. It is very probable that Q_7 will differ for different antioxidants, and it is possible that Q_6 will vary for different types of vulcanizates. What is observed of course in accelerated aging tests is that antioxidants become less effective with increasing temperature as far as preservation of tensile strength is concerned.

If the rate of attainment of the photostationary state is measured under different conditions of light intensity and temperature, it should be possible from the values of the constants obtained to calculate the rate of oxidation of the rubber under any specified conditions of temperature and intensity of light. It is possible to assess preferred values of E, *viz.*, $k_6+k_7f(i)$, and $E\times D$, *viz.*, $k_3\{k_4'+k_8'f(I)\}$, for different aging conditions. For vulcanizates which under normal service conditions do not come under the influence of light, such as inner tubes, it is important that E is as large as possible. On the other hand, the lowest possible value of $E\times D$ is desirable in vulcanizates such as bathing caps which will be exposed to bright sunlight.

The use of oxygen consumption measurements for foretelling the aging characteristics of rubber vulcanizates has been recommended by Dufraisse[17] and others.

A determination of the rate of oxidation at one temperature will have some of the drawbacks of the usual accelerated aging tests with none of their advantages. The disadvantages of single temperature measurements when the values of Q vary so considerably have already been pointed out. In addition it has been shown that the rate of oxidation over the first hours at elevated temperatures are markedly affected by the immediate previous history of the rubber, and a considerable error may be introduced because of this. In the other accelerated tests, in the Geer oven and to a lesser extent in the oxygen bomb, the measurement of the deterioration is taken over a longer period, and the errors due to this factor will not be so pronounced.

2. The Dimensions of the Oxidizing Sample.

The approximate formula for the equilibrium value of the depth of oxygen penetration into a sheet of rubber was shown to be $d=\sqrt{\dfrac{2Pp}{\rho k}}$.

This may be rewritten in the form $d=\sqrt{\dfrac{2P'p}{\rho k'}}\cdot e^{Q-Q'/2RT}$

where P' and k' are the temperature-independent portions of the permeability and oxidation constants. Since k depends on the nature and amount of antioxidant present it will be seen that the depth of oxygen penetration will vary under the same testing conditions according to the efficiency of the antioxidant in the rubber.

The more effective the antioxidant (*i.e.*, the slower the ideal rate of oxidation) the greater will be the depth of penetration d. Since Q is larger than Q', the quantity $e^{Q-Q'/2RT}$ will decrease with temperature, and consequently d will decrease exponentially with increase of temperature.

It can thus be seen that a rubber article may oxidize throughout its mass when kept at room temperature, whereas if the temperature is increased it may oxidize only in the superficial layers and, according to whether an antioxidant is present or not, the depth of this oxidizing layer will vary. This may be a factor which should not be ignored when comparing Geer oven and dark aging measurements.

To illustrate how this factor may influence the relative value of dark aging and Geer oven aging for assessing an antioxidant, suppose the thickness of the test-piece and the rates of oxidation are such that at ordinary temperatures the value of d is large enough to ensure that oxidation proceeds throughout the mass of the rubber in the samples with and without antioxidant. If the deterioration in properties is a function of the amount of oxidation, and this function is not affected by the presence of antioxidant, then the relative rates of decrease in tensile strength of the two samples will be a measure of the protection afforded by the antioxidant against oxidation.

If at 70° C. in the Geer oven the value of d is decreased to such an extent that the interior of the first test-piece does not oxidize at first, then a different ratio will be obtained between the rates of fall of tensile strength because oxidation in the early stages will be confined to different depths of rubber according to whether antioxidant is present or not. The value of d will be smaller in the test-pieces containing no antioxidant, and the tendency to localize oxidation in the surface layer of the unprotected mix will result in the outside layer combining with more than the 1% of oxygen that is required to destroy its tensile strength. There will therefore be a tendency towards an inefficient utilization of the oxygen the smaller is the value of d. The antioxidant will thus not show up to such effect at temperatures where uneven oxidation occurs, and the higher the temperature the less effective will the antioxidant appear.

It is conceivable that under certain conditions at high temperatures of testing in the Geer oven, the sample with the antioxidant might appear to perish more rapidly than the unprotected sample, and hence give an entirely wrong picture of the efficacy of the antioxidant.

Tener and Holt[18] have measured the efficiencies of antioxidants by comparing aging curves with and without a variety of antioxidants under different conditions. They state that the order of decreasing effectiveness of antioxidants is as follows:

1. Dark storage.
2. Oven at 70° C.
3. Oven at 90° C.

This is the order of effectiveness one would expect if depth of oxygen penetration is the major factor.

If the oxygen pressure is increased, the value of d increases with the square root of the oxygen pressure p. This means that in an oxygen bomb the value of d will be large and oxidation will proceed throughout the sample. Thus there is a similarity between oxygen bomb aging and dark aging as far as homogeneity of oxidation is concerned. As samples exposed to light oxidize more quickly at the surface, there is a similarity in the lack of homogeneity of the oxidation under these conditions and in the Geer oven aging at high temperatures. It is interesting to note again that Tener and Holt indicate that the best method of assessing

antioxidants for protection against exposure to weather is the Geer oven at 70° and 90° C., whereas the oxygen bomb correlates more closely with dark aging.

It is very unlikely that the presence of the antioxidant will affect the nonhomogeneous oxidation rate by affecting the permeability coefficient P, and therefore no complications need be expected on this score.

It is interesting to note that a reduction in the permeability will result in a decreased depth of oxygen penetration and a corresponding decrease in the rate of consumption of oxygen by the rubber.

Generally speaking, no significant decrease in permeability of vulcanized rubber can be effected by additions of minor quantities of other substances (Morris[19]) and consequently it is unlikely that the rate of oxidation of rubber at high temperatures can be appreciably reduced by the physical process of making it more difficult for the oxygen to diffuse into the rubber.

The difference in aging characteristics between two different technical mixes may be due in part to differences in permeability, which will be accentuated when testing in the Geer oven at high temperatures.

One of the factors in the remarkable resistance of Neoprene to oxidation, particularly at high temperatures, must be ascribed to its low permeability, which is only 20% of that of natural rubber.

3. Oxidation of the Antioxidant.

There is practically nothing known about the fate of the antioxidant in perished rubber. A. G. Murray, working in the laboratories of Imperial Chemical Industries, Limited, has obtained indications of progressive disappearance of β-naphthol in a rubber vulcanizate aged in an oxygen bomb.

The antioxidant may disappear as a consequence of two types of oxidation, *viz.*:

(*a*) the chain-ending mechanism, which is independent of oxygen pressure,

$$RO_2^* + i \xrightarrow{k_7} \text{deactivated products,}$$

and

(*b*) a direct oxidation by molecular oxygen, which probably varies with the oxygen pressure,

$$i + O_2 \longrightarrow \text{oxidized products.}$$

The possibility of (*a*) removing antioxidant has already been discussed. The direct oxidation of the antioxidant by molecular oxygen is to be expected, particularly under the conditions prevailing in the oxygen bomb. Williams and Neal have indicated that they believe this to be one of the reasons for the increased rate of deterioration observed under high oxygen pressure. The destruction of the antioxidant would be increased in proportion to the increase in the oxygen pressure, whereas the destruction of the rubber would be independent of the oxygen pressure. Thus an antioxidant susceptible to direct oxidation would show up badly in the oxygen bomb, although it might be an excellent antioxidant under normal conditions.

Bierer and Davis[20] have pointed out that the time-tensile strength curves obtained in oxygen bomb aging often show a sudden increase in the rate of tensile strength fall. This effect is to be expected if direct oxidation of the antioxidant is an important feature of aging under these conditions. This autocatalytic effect observed in the oxygen bomb can be regarded as an enhanced Kohman effect. Under pressures of one atmosphere of oxygen disappearance of antioxidant is not marked until about 20-50% of the rubber has perished, whereas

if the relative rate of oxidation of the antioxidant to that of rubber is increased by increasing the oxygen pressure a hundredfold the autocatalytic effect due to disappearance of antioxidant becomes apparent in the first 1% of the oxidation range where tensile strengths are still measurable.

The factor

$$\frac{\text{antioxidant disappearance due to direct oxidation}}{\text{antioxidant disappearance due to chain-ending}}$$

which we will term γ will vary considerably with the oxidizing conditions. High oxygen pressure will favor a high value of this ratio and therefore $\gamma_{\text{(oxygen bomb)}}$ will be greater than $\gamma_{\text{(Geer oven)}}$.

The values of γ for oxidation at normal temperatures in the dark and in the light will also be different. In the case of the sample exposed to light, more chains will be initiated and subsequently stopped by antioxidant and this will result in a lower value of $\gamma_{\text{(light)}}$ when compared with $\gamma_{\text{(dark)}}$.

The importance of a knowledge of the variation in this factor when attempting to correlate the results of accelerated aging tests with aging under specific service conditions is obvious, but no attempts have been recorded in the literature to measure either this factor or the closely related quantity,—the rate of oxidation of the antioxidant by gaseous oxygen.

4. THE MOBILITY OF THE ANTIOXIDANT.

A remarkable feature of rubber autoöxidation is its relative indifference to antioxidant action. The protection afforded by the best antioxidants is equivalent to a retardation coefficient of a few units only, despite the fact that the search for antioxidants for rubber has been probably more intensive than for any other substance. The introduction of antioxidants into other autoöxidizing systems quite commonly results in a hundred- or thousand-fold reduction in the rate of oxidation, and Dufraisse[17] has recorded a retardation coefficient of as much as 1,000,000 for benzaldehyde stabilized by 1% of hydroquinone.

There are two possible reasons for this, viz.:

(*a*) the reaction chain length of rubber oxidation in the absence of antioxidants is small, and

(*b*) the mobility of the antioxidant molecule in the vulcanized rubber structure is restricted.

The rate of oxidation is equal to the rate of chain initiation multiplied by the chain length and an antioxidant decreases the oxidation rate by decreasing the chain length. In the case of autoöxidation of benzaldehyde exposed to light, Bäckström[21] has shown that the chain length is between 5000 and 10,000. Thus, the addition of an antioxidant which will reduce this chain length to 1 effects a corresponding decrease in the rate of oxidation. If in rubber the chain length in the absence of antioxidant is small then the retardation coefficient possible is correspondingly small.

A restricted antioxidant mobility will play a part also in making the antioxidant less effective. A molecule of peroxide in a mobile autoöxidizing system like benzaldehyde will have thousands of fruitless collisions with benzaldehyde molecules before the propagation reaction step takes place resulting in the oxidation of a benzaldehyde molecule. This propagation reaction step will repeat itself according to Bäckström's figures, 5000 to 10,000 times before the peroxide molecule disappears. If antioxidant is added to the system so that there is, say, 1 molecule of antioxidant to every 100 molecules of benzaldehyde, then on the

average every hundredth collision of the peroxide molecule will be one with an antioxidant molecule. If the antioxidant is very efficient, that is it will deactivate a peroxide molecule practically every time it becomes involved in collision with it, then the chances are that the peroxide will be deactivated before it can undergo even the first chain-propagating step. There is thus a reduction of the chain length from between 5000 and 10,000 to 1 with a proportional decrease in the rate of oxidation.

In the case of rubber, the peroxide is part of a macromolecular structure and can collide only with double bonds in its immediate vicinity. The antioxidant molecule may be some distance away, and will only diffuse through the rubber very slowly. There will therefore be a tendency for the propagation reaction chain to proceed rather than to await the arrival of the antioxidant molecule. In the extreme case where the diffusion of the antioxidant is slow compared with the movement of the peroxide reaction path, the antioxidant may be regarded as immobile. A peroxide formed in the rubber structure some distance from an antioxidant molecule will propagate and continue to do so until its reaction path brings it into the neighborhood of the antioxidant molecule.

This is probably the reason why rubber antioxidants have to be used in such high concentrations compared with those used in connection with the protection of mobile liquids. Furthermore, it is probably the explanation of why certain antioxidants are relatively ineffective at low concentrations. A very excellent example of the importance of mobility in an antioxidant is shown by comparing the activities of aldolnaphthylamines and diphenylamine. Used at normal concentrations the aldolnaphthylamines product is very much more effective than diphenylamine, but when used at a concentration of one-tenth of one per cent (by master batching) the diphenylamine is the more effective antioxidant.

	A	B	C
Smoked sheet	100	100	100
Zinc oxide	5	5	5
Gas black	47.5	47.5	47.5
Stearic acid	3	3	3
Sulfur	3	3	3
Mercaptobenzothiazole	0.85	0.85	0.85
Aldolnaphthylamines	—	0.1	0
Diphenylamine	—	—	0.1

All vulcanized for 45 minutes at 141° C.

	Tensile strength (kg. per sq. cm.)	Elongation (%)
A, B, and C before aging	247	540
A after 1 day in bomb (70° C. and 300 lbs.)	68	309
B " " " " " (" " " ")	80	335
C " " " " " (" " " ")	150	467

Consider a rubber vulcanizate containing 1% of a normal rubber antioxidant and assume that (*a*) it is completely soluble in the rubber and it exists as unaggregated molecules, (*b*) it has practically no mobility in vulcanized rubber, and (*c*) it is capable only of exerting a protective action on the double bonds in its immediate vicinity (say 2 double bonds for the sake of illustration). Then it can be shown simply that at only 1 double bond out of 100-200 bonds can the antioxidant exert its chain ending influence. If the antioxidant is completely efficient, *i.e.*, it will always stop a chain when it reaches its proximity, then the

minimum average chain length will be between 100 and 200. The smaller this chain length can be made, the more effectively is the rubber protected against oxidation. This may be achieved by adding more antioxidant, but the limit to this is governed by the true solubility of the antioxidant in the rubber. Above this limit the excess over the solubility will exist in the form of aggregates and will have only a small effect on the chain length or rate of oxidation.

This is the reason why with most antioxidants their effectiveness falls off rapidly with increasing concentration. Where, however, the effective solubility is increased by high temperatures in use, *e.g.*, truck inner tubes, then greater percentages of antioxidant can be effectively used. By this is meant that 5% on the rubber will be more effective than 4%, whereas for use in rubber kept at the ordinary temperature 5% would be no more effective than 4%, or possibly even than 2%, but it must be remembered that owing to the decreasing effectiveness of antioxidants with increasing temperature, it is probable that 5% at higher temperatures may be relatively less effective than 1% at lower temperatures.

The most effective method of protecting rubber from oxidation would be to place an antioxidant molecule alongside each double bond. This, of course, is impossible, not only because of the limits set by the solubility of the antioxidant in the rubber, but also because the resulting mixture would possess very little resemblance to rubber. The chlorine atom attached to the double bond carbon atom in Neoprene reduces the anionoid reactivity of the double bond and will therefore have a similar effect to placing each double bond under the protection of an antioxidant molecule. There seems little doubt that this is the main reason for the remarkable resistance of Neoprene to oxidation and to the action of ozone.

SUMMARY

1. An apparatus is described for the measurement of the rate of oxidation of rubber at either constant pressure or constant volume. Provision is made for further additions of oxygen during the oxidation.

2. It was confirmed that the rate of oxidation of rubber is independent of the oxygen pressure.

3. The zero order reaction rate of oxidation varies with temperature according to the Arrhenius equation.

4. The depth of oxygen penetration decreases exponentially with temperature, and is reduced by low oxygen pressure, low oxygen permeability or by a fast rate of oxidation.

5. If the dimensions of the rubber sample are too large, or the temperature is too high, it is probable that only the outside layers of the rubber will undergo oxidation, and the low rate of oxidation observed will depend on the depth of oxygen penetration.

6. On exposure to light the propensity of the rubber for oxidation gradually increases, and the data suggest the slow attainment of a photostationary state between two opposing reactions, involving the formation of peroxide by light and disappearance by a dark reaction.

7. On removing light-activated rubber into the dark, the enhanced oxidation rate persists for a considerable time.

8. All specifications for accelerated aging tests should specify the importance of not exposing the samples to a bright light before submitting them to the aging operation.

9. The peroxide formed by the action of light can be destroyed by the action of heat *in vacuo*.

10. The most probable interpretation of the data available on the effects of oxygen pressure, temperature and light is that the oxidation of rubber is similar to other autoöxidations in being a chain reaction.

11. The autocatalytic nature of the oxidation of vulcanized rubber is not apparent over small ranges of the oxidation, and it is suggested that the gradually increasing rate is due to the disappearance of antioxidant.

12. Raw rubber on the other hand shows a marked induction period, followed by an accelerating rate of oxidation clearly discernible over even very small ranges of oxidation. It is considered that this is due to the development of the reaction chains in time.

13. Antioxidants can be accurately evaluated only by service tests, since the factors affecting the efficiency of antioxidants are the depth of oxygen penetration into the rubber, the rate at which the antioxidant itself may disappear by oxidation, and the mobility and solubility of the antioxidant. Accelerated aging tests take no account of these factors, which vary with different aging conditions. Furthermore, since the Arrhenius constant Q and consequently the temperature coefficient of the oxidation, vary with the nature of the vulcanizate and the antioxidant addition, measurements at one elevated temperature will not give true indications of the relative rates of oxidation at the ordinary temperature.

The authors are indebted to E. K. Rideal for several stimulating discussions on the theoretical aspects of autoöxidation, to R. F. Goldstein for advice in certain aspects of the work, to S. Mottram for carrying out many accelerated aging tests in connection with this work and to Imperial Chemical Industries, Ltd., for permission to publish the results embodied in this paper.

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MEASUREMENT OF THE ABSORPTION OF OXYGEN BY VULCANIZED RUBBER IN AIR *

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INTRODUCTION

The problem of estimating the aging quality of a vulcanized rubber compound by short period tests is one of considerable difficulty, and various attempts have been made to devise trustworthy and convenient methods for accelerating and assessing the deterioration of the rubber.

It is generally agreed that oxidation is the main cause of decay in rubber, and most of the means in common use for accelerating the decay act mainly by accelerating oxidation. These include the Geer-Evans test in which the rubber is stored in air at 70° C. (158° F.), the Admiralty dry-heat test in air at 180° F. (82.2° C.), and the Bierer-Davis oxygen-bomb test at 70° C. (158° F.) in oxygen at a pressure of 300 lbs. per sq. inch.

In the Geer-Evans and the Admiralty dry-heat tests, oxidation is accelerated by raising the temperature, and in the Bierer-Davis oxygen-bomb test by increasing the oxygen concentration as well as the temperature.

The decay of rubber is reflected in many of its properties, but the one most commonly measured as an index of decay is the tensile strength. It may be measured in unaged samples and in samples subjected to accelerated aging for increasing times, in which case the results are expressed in a tensile strength/time curve. This elaborate procedure is desirable in most investigational work, but for routine and comparative tests it is usually sufficient to age the rubber for one fixed period and to measure the initial and final strengths. Naturally, in order to obtain good differentiation among rubbers of different aging qualities, the duration of the accelerated aging period must be such that all will lose appreciable fractions of their initial tensile strengths.

A few years ago aging periods of about a week in the air oven or a few days in the oxygen bomb would produce sufficient fall in tensile strength for the aging qualities to be compared. Recent advances in rubber technology have resulted in great improvements in aging qualities, and it is no longer possible in short period air oven or oxygen-bomb tests to discriminate between the better mixes. The aging periods must be considerably lengthened, and the inconvenience of this makes it desirable to develop a shorter laboratory aging test which will still correlate well with natural aging.

The time of aging can be reduced by raising the temperature, but this is apt to impair the discrimination between good and bad rubbers, and may even place rubbers in the wrong order of merit.

Aging in the bomb could be hastened by increasing the oxygen pressure, but to halve the time it would be necessary, roughly speaking, to quadruple a pressure already inconveniently high and so greatly to increase the danger of explosion from spontaneous combustion.

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New methods must therefore be explored if it is desired to assess the aging properties of rubbers by short period tests.

Previous investigators[1] have found that there is good correlation between the rates at which oxygen is absorbed by different rubbers suspended in pure oxygen and the decay in their tensile strengths in air at the same temperature, and have suggested that this test might be considered as an alternative when the preparation of tensile test-pieces is difficult or impossible. A test of this nature can yield results in a few days.

The technique involved in filling a tube with pure oxygen is rather cumbersome and unsuitable for routine testing, and by using air instead of oxygen the technique can be greatly simplified. The authors have therefore designed an apparatus for the measurement of oxygen absorbed by rubber in air.

DESCRIPTION OF APPARATUS

The rubber specimen is hung in a graduated glass tube in air over mercury. The enclosed space can be adjusted to atmospheric pressure and measured. (Fig. 1.)

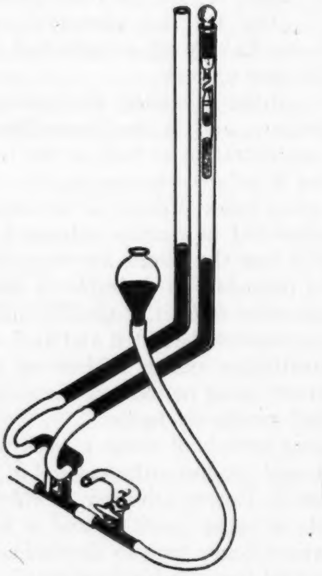

FIG. 1.—Oxygen absorption tube.

The complete apparatus (Fig. 2) consists of a number of such tubes, closed at the top by ground glass stoppers with mercury seals. The rubber specimens are hung from the stoppers. The bottom of each graduated tube is connected to an open-topped auxiliary tube mounted beside it, and any pair of tubes can be connected through a tap to a common reservoir of mercury, the level of which can be altered by means of a coarse adjustment ratchet and a fine adjustment screw. The tubes are mounted in a glass-fronted air thermostat and are attached to the inside of the door, the taps and the reservoir being mounted on the outside of the door.

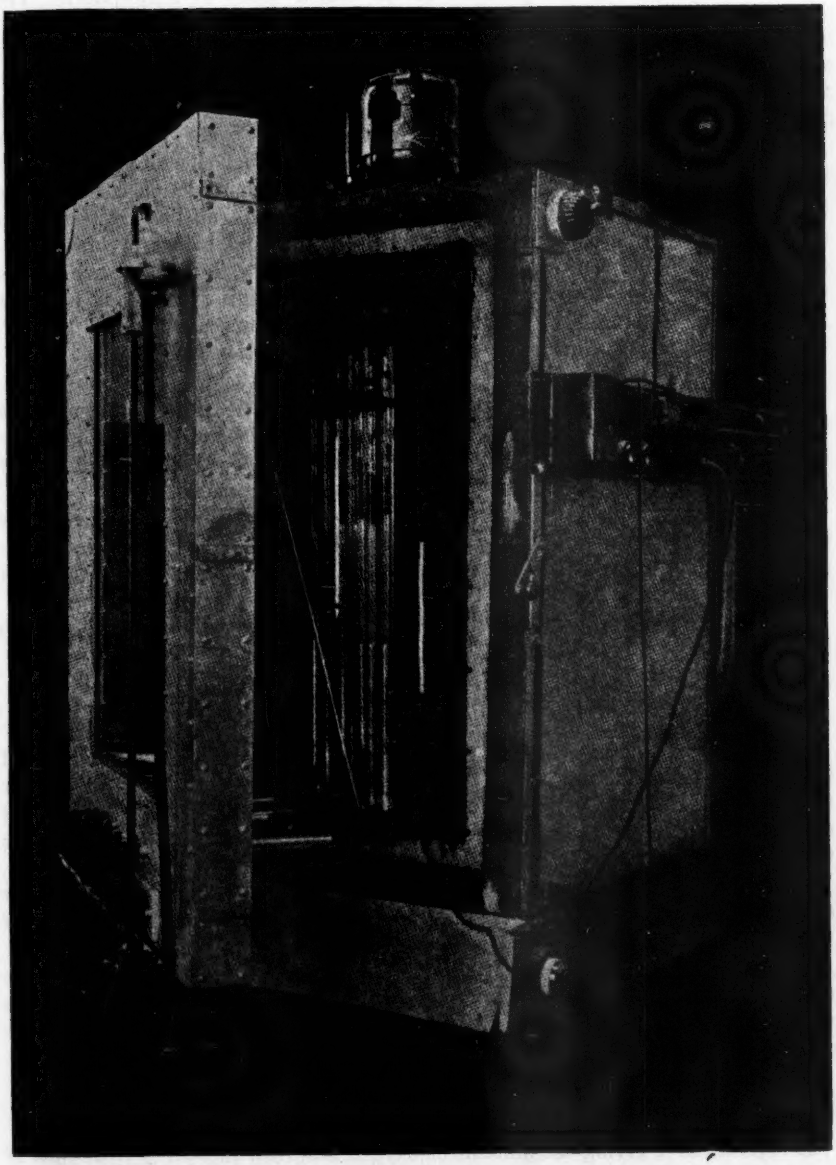

FIG. 2.—Oxygen absorption apparatus.

A vertical mirror is mounted on the back wall of the oven to facilitate the operation of adjusting the pressure in the sealed tubes to atmospheric. The readings are corrected to N.T.P.

The air thermostat[2] is a double-walled box about 2 ft. by 2 ft. by 3 ft. internally, with heavily lagged outer walls and thin sheet steel inner walls.

Air is drawn by an electric fan out of the top of the oven and circulated by a system of baffles through the space between the double walls, in which heating elements are placed, to re-enter the oven eventually through slits along the bottom edges of the side walls. The principle underlying this construction is that if the boundary walls are maintained at a desired temperature no body within them can attain—by conduction, radiation, or convection—any higher or lower temperature, and in spite of some obvious departures from the ideal (such as the unheated door of three separated sheets of plate glass) this oven has an excellent performance. Temperature gradients are almost eliminated, and at 180° F. (82.2° C.) the maximum error in the space occupied by the tubes is about 0.2° F. (0.1° C.).

In all aging tests, accurate temperature control is essential because of the sensitivity of the reaction velocity to temperature changes, but it is doubly necessary here, for in a gas volume of 50 cc. an error 0.1° C. involves a change of 0.01 to 0.02 cc., which is of the same order as the reading error.

There are two heating circuits—one, in series with an adjustable rheostat, is capable of maintaining the temperature about 10-15° C. below the desired temperature; the second supplies the remainder of the heat, and is controlled by an enclosed mercury relay operated by a toluene-mercury thermo-regulator.

At 180° F. (82.2° C.) the total consumption of the thermostat is about 800 watts.

EFFECT OF MOISTURE IN THE RUBBER

Preliminary experiments made at 180° F. (82.2° C.) showed that, after all available oxygen had been absorbed, the volume of the residual gas was larger than it should have been and even tended to increase with time. Evolution of carbon dioxide was naturally suspected, but analysis showed that only negligible traces were present and that the increase in volume was due to water vapor. Water vapor was found to be evolved most rapidly in the early stages of the test and is more probably moisture originally present in the rubber than a product of reaction.

The trouble was overcome by hanging the specimens in the oven outside the tubes overnight to remove most of the moisture, and by including a small glass vessel containing phosphorus pentoxide in each absorption tube with the specimen.

FORM OF THE OXYGEN-ABSORPTION/TIME CURVES

A typical curve giving the amount of oxygen absorbed plotted against time of test is shown in Fig. 3.

The tubes contain about 50 cc. of air at the beginning of the test, so approximately 10 cc. of oxygen are available for absorption by the rubber. In the example given, the initial volume of air was 44.75 cc., so 9.4 cc. of oxygen were available for absorption.

It will be seen from the curve that the changing oxygen concentration does not affect the rate of absorption appreciably, as the curve is sensibly a straight line until most of the oxygen is exhausted. It is known that autocatalysis tends to increase slightly the rate of oxygen absorption as oxidation proceeds, but even when allowance is made for this fact analysis of the curves suggests that the rate of absorption is very nearly proportional to the square root of the concentration. This is a surprising result, the reason for which is by no means obvious but which is undoubtedly very convenient for this type of test.

The initial slope of the curve is taken as a measure of the rate of oxygen absorption, which is expressed as milliliters of oxygen per hour per gram of rubber (mix or hydrocarbon) at the test temperature.

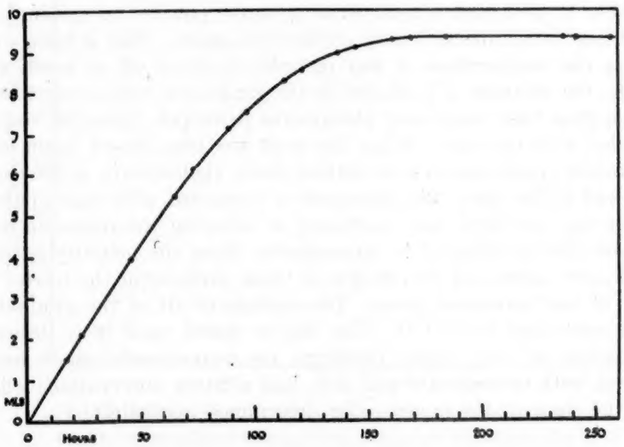

FIG. 3.—Typical oxygen absorption curve.

INFLUENCE OF THE SURFACE/VOLUME RATIO ON THE RATE OF OXYGEN ABSORPTION

The chemical reaction between rubber and oxygen increases with temperature much more rapidly than does the physical process of diffusion of oxygen through rubber. Consequently diffusion, which is normally unimportant at ordinary temperatures, may at high temperatures easily become the limiting factor in oxygen absorption, because the outer layer of rubber reacts with the oxygen as fast as it diffuses in and the interior of the rubber is starved and inactive.

In order to investigate the magnitude of this effect the influence of the surface/volume ratio on the rate of oxygen absorption was determined on two rubber compounds.

One was a tough rubber compound containing 43% rubber, 42% siliceous matter, 9% carbon black, paraffin wax, sulfur, and an antioxidant.

The other was a soft rubber compound containing 57% rubber, 40% zinc oxide, and the remainder sulfur.

Samples of these rubbers having surface/volume ratios ranging between 7 and 70 (cm. units) were prepared from thick sheets by grinding, and powdered samples having a very high, though unmeasured, surface/volume ratio were prepared by rasping, and their rates of oxygen absorption were measured.

The rate of absorption increases as the surface is increased, rapidly at first when the surface is small, and finally very slowly when the surface is large. When the surface is greater than 50 sq. cm. per cc. the change becomes negligible.

If the oxygen-absorbing properties of two rubbers are to be compared, it is essential that the surface/volume ratios of the two rubbers be equal, or so high that the difference between them will not affect the rate of oxygen absorption. As it is easier to make the surface/volume ratio high than to work with a small fixed ratio, and as the latter, to be satisfactory, requires also a constant rate of diffusion, rasped rubber samples were used for all the oxygen absorption tests.

METHOD OF CARRYING OUT THE TEST

The rubber to be tested is reduced to a coarse powder by rasping[3]. A sample is weighed into a cylindrical basket of fine iron gauze. This is hung overnight in the oven at the temperature of test in order to drive off as much moisture as possible. In the morning it is placed in the graduated tube, suspended, together with a little glass tube containing phosphorus pentoxide, from the stopper, which is then sealed with mercury. When the oven has been closed again long enough for temperature conditions to have settled down, the mercury in the closed graduated tube and in the open tube alongside is connected with that in the reservoir through the tap provided, and by raising or lowering the reservoir the pressure in the closed tube is adjusted to atmospheric, when the mercury surfaces in the closed and open tubes and the images of those surfaces in the mirror behind lie accurately in one horizontal plane. The volume of air in the graduated tube is noted and converted to N.T.P. The tap is closed until it is desired to take another reading on that tube. Readings are conveniently taken morning and evening, and, with normal care and skill, half a dozen observations will be ample to enable the slope of the curve to be determined accurately.

OXYGEN ABSORPTION AND TENSILE DECAY

When the aging of rubber compounds is accelerated by raising the temperature there is commonly an initial increase in tensile strength followed by a gradual decrease. It is the rate of this decrease in tensile strength that determines whether the rubber has good or bad aging qualities, and for this reason most accelerated aging tests are made sufficiently long to outweigh the effect of the initial rise.

As a rule the decrease begins not later than in the second day's aging. Thereafter the tensile strength falls at a fairly uniform rate for a period measured in weeks, and finally approaches asymptotically the low strength of fully perished rubber.

As the fall in tensile strength between 2 and 9 days was moderately linear in all the rubbers examined, we have adopted the percentage fall in this period as an arbitrary measure of tensile aging quality, and in Fig. 4 this value is plotted against rate of oxygen absorption for 41 different rubbers. These rubbers include tough rubber cable sheathings, insulant rubbers, flooring rubbers, soft rubbers, rubbers for suction hose and rubbers to Government Department Specification T.G. 25A, Qualities C and D.

It will be seen that the correlation between the two methods of expressing rate of deterioration is remarkably good. There is, inevitably, a considerable scattering of the experimental points about the ideal straight line—that is, unless their aging

qualities are very different, the rubbers are not always placed in the same order of merit by the two methods—but the agreement is closer than might have been expected, and, in so far as there is disagreement, the authors believe that oxygen absorption is a more fundamental and probably a more trustworthy index of general decay than the nonlinear changes in any one physical property.

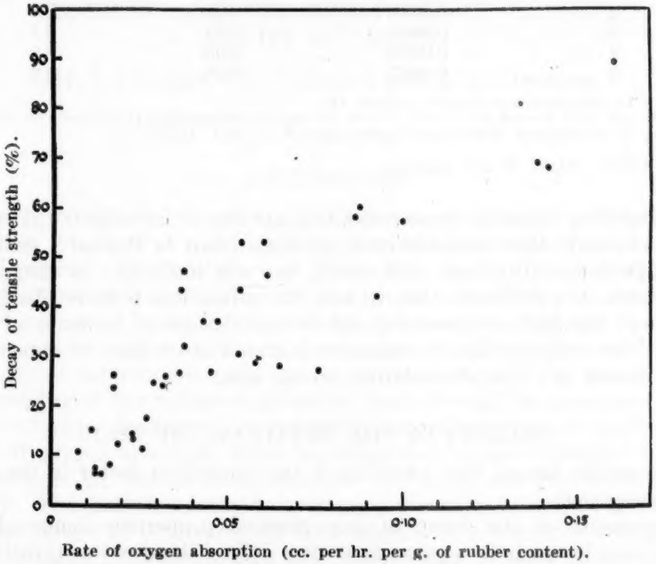

FIG. 4.—Correlation between oxygen absorption and tensile decay.

OXYGEN ABSORPTION IN AIR AT 100° F. (37.8° C.)

Doubt always exists whether the results of an accelerated aging test give a trustworthy indication of the probable life of a rubber in service. Experiments (unpublished) were carried out some years ago by F. B. Young at the Admiralty Research Laboratory, Teddington, in which a number of rubbers representative of cable insulants were subjected to tensile aging tests at a series of temperatures between 150° F. and 270° F. These showed very clearly that differences in the aging qualities were progressively reduced as the aging temperature was raised; discrimination between good and bad rubbers was very poor at 270° F. and best at 150° F., and there is little doubt that at normal atmospheric temperatures the differences in aging qualities would have been still more marked.

The necessity for completing a test in a reasonable time precludes the adoption of a low temperature for routine tests based on tensile decay, but with the apparatus now described it is possible to measure the rates of oxygen absorption at temperatures only slightly above natural aging temperatures, and to obtain results in a few weeks at most.

The effects of antioxidants and other compounding ingredients on the natural aging of rubber compounds can therefore be measured directly and in a comparatively short time without the somewhat dubious conversion from tests at high temperatures.

The results of a few tests made at 100° F. are given in the table below together with the results obtained at 180° F.

Rubber	Rate of oxygen absorption in air (cc. per hr. per g. of rubber content) At 100° F. (37.8° C.)	At 180° F. (82.2° C.)	Factor for 10° C.
1	0.0009_4	0.08_8	2.8
2	0.0001_7	0.03_7	3.4
3	0.0006_5	0.05_4	2.7
4	0.0003_9	0.05_3	2.9
5	0.0007_8	0.16_0	3.3

1. Rubber to Admiralty Specification pattern 8B.
2. " " " " " " plus an antioxidant.
3. Rubber to Government Department Specification T. G. 25A. Quality C.
4. " " " " " " " D.
5. 60% Rubber, details of mix unknown.

One subsidiary object of these measurements was to investigate the contention of a manufacturer that the addition of an antioxidant to Rubber 1 enabled it to pass a high-temperature test with credit, but was ineffective at normal service temperatures. It will be seen that, in fact, the antioxidant is more effective at the low than at the high temperature, and in the absence of evidence to the contrary—as, for example, that its influence is transient—it may be concluded that the antioxidant is a valuable addition to the mix.

SUMMARY OF THE MERITS OF THE TEST

It is generally agreed that oxidation is the controlling factor in the decay of rubber compounds.

Measurements of the decay of any physical properties—commonly tensile strength—can be made in a convenient time only if the decay is greatly accelerated, and there is always a grave doubt about the equality of the acceleration for different materials. There is also a difficulty in selecting a universally suitable aging period, since the decay of the physical properties is not linear.

A direct measure of the rate of oxidation is, in our view, more fundamental and less equivocal. It can, moreover, be made in a reasonable time at a temperature not far removed from service temperatures.

Again, whereas tensile tests require several samples of each point in the time-curve to give acceptable mean values, here a single sample suffices for the whole test, and this sample can be simply prepared from a specimen of any form by rasping.

The merits and simplicity of the method should commend it to rubber technologists.

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[2] In principle essentially similar to that described by Evans, *Chem & Ind.* **50**, 66 (1931).
[3] Doubt was felt lest the rasping should damage the rubber or in some way change its chemical stability, but in none of the experiments was any evidence of damage observed.

THE DIRECT DETERMINATION OF OXYGEN IN RUBBER *

THE ADAPTATION OF THE TER MEULEN METHOD TO RUBBER AND ITS APPLICATION TO THE STUDY OF AGING

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INTRODUCTION

The study of the deterioration of rubber as an oxidation phenomenon has engaged the attention of many investigators, and has resulted in hundreds of published papers[1]. This profusion of publications on the subject would seem to render further research in this phase of the chemistry of rubber unnecessary. However, in this mass of literature no reference has been found to any work dealing with the direct determination of combined oxygen in rubber. The usual approach to the study of the rubber-oxygen system has been through the measurement of the oxidizability of the rubber stock rather than through the measurement of its state of oxidation. Dufraisse[2], in discussing the measurement of oxidizability or quantity of oxygen absorbed, which he terms the "oxygen number," lists three major methods for its determination: the analytical, the gravimetric and the volumetric. The analytical method, involving combustion for carbon and hydrogen to give the oxygen by difference, has been adapted to raw rubber with great precision by Midgley, Henne, Shepard and Renoll[3], and to the examination of the alcoholic potash extract of aged vulcanized rubber by van Rossem and Dekker[4]. If this method could be adapted to compounded stocks with the accuracy attained by these investigators, it would become a measure of the state of oxidation. It is, however, time-consuming and, as an indirect method, subject to cumulative errors. The gravimetric or increase-in-weight method, though being the simplest, is open to large inherent errors, the major one resulting from the loss of volatile products of oxidation. The volumetric method involves the measurement of the volume of gaseous oxygen absorbed by the sample of rubber at a given temperature and at either constant pressure or variable pressure (manometric). Dufraisse and his coworkers have made the greatest contributions in the development of this method[2]. Kohman[5] applied the constant-pressure method to the study of the relation of oxygen absorption to natural aging. Although this method is accurate, and with the proper apparatus allows multiple simultaneous determinations, it has been limited to the study of oxidation at relatively low oxygen pressures. Furthermore, being essentially a measure of oxidizability, it can be applied in no way in the determination of the state of oxidation of already aged specimens of rubber.

The present investigation, of which this paper is a preliminary report, was undertaken because of this lack of a method for the direct determination of combined oxygen in samples of rubber of known or unknown history.

The methods which have been studied for the direct determination of oxygen in organic compounds have been capably reviewed by Kirner[6]. Of these various

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methods, and particularly of those proposed during the past decade, that of ter Meulen[7, 8] improved by Russell and coworkers[9, 10, 11], stands out as the simplest and the most reliable. This method, applicable originally to organic compounds containing only carbon, hydrogen and oxygen, consists essentially in volatilizing the sample in a stream of hydrogen which flows over a hot cracking catalyst, and over a reducing catalyst, to give methane and water as final products. Russell and Marks[10] adapted the method to nitrogen-containing compounds, and Marks[11] added further changes to make it applicable to compounds containing small percentages of sulfur, a qualification which is of vital consideration in the analysis of vulcanized rubber. Van Rossem and Dekker[4] abandoned the attempt to apply the original ter Meulen method to the analysis of the alcoholic potash extract from aged vulcanized rubber because of difficulties resulting from the sulfur present.

In the present work the basic principles and procedure of Marks[11] have been modified further to meet the special requirements encountered in the determination of oxygen in rubber. The resulting adaptation has been applied (*a*) to the determination of combined oxygen in vulcanized rubber aged in the Geer oven[12] and in the Bierer-Davis oxygen bomb[13], and (*b*) to the study of the correlation of combined oxygen with antioxidant efficiency.

METHOD AND APPARATUS

In applying the method of ter Meulen to vulcanized rubber two difficulties soon become apparent. Firstly, the reducing catalyst is subjected to greater quantities of sulfur than Marks encountered, whereby its effective life is materially shortened. Secondly, the life of the cracking catalyst is greatly reduced by its surface becom-

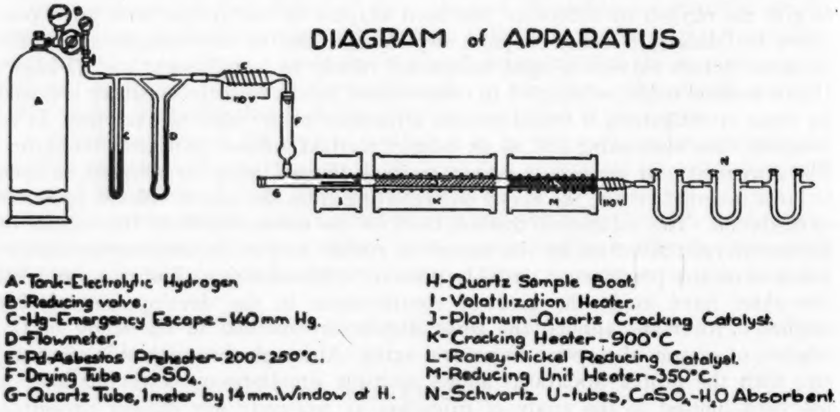

FIG. 1.—Diagram of apparatus.

ing choked with a voluminous deposit of carbon which results from the pyrolysis of the rubber hydrocarbon. The use of relatively large samples of rubber, *i. e.*, one gram, because of the low percentages of oxygen to be determined, aggravates these troubles.

The first difficulty can be solved in some degree by using a more rugged reducing catalyst containing a very high proportion of nickel. Such a catalyst is that invented by Raney[14]. This catalyst is prepared by treating an alloy composed of equal parts of nickel and aluminium with aqueous sodium hydroxide, which dis-

solves out the aluminium leaving a very porous type of nickel[15]. Because of its large surface area and high concentration of active nickel, it is able to accept relatively large quantities of sulfur and thus remain active for a reasonable number of determinations. Little success was attained in overcoming the effect of the carbon deposit. The temperature of the cracking catalyst was raised from 750° C., as recommended by Marks[11], to about 900° C. However, it cannot be stated definitely that this effected any marked improvement. Increasing the concentration of platinum on the surface of the silica somewhat increased the life of this catalyst.

The apparatus used was essentially the same, with minor modifications, as that described by Marks[11], and is shown in Fig. 1. Resistance heaters were used throughout. A three-section organic combustion furnace was used to heat the quartz tube containing the catalysts. The temperatures in the first two heating units, I and K, were controlled by hand-operated rheostats which had previously been calibrated by thermocouple. The temperature in the last unit, M, was regulated more accurately by means of a Leeds and Northrup potentiometric controller-recorder and maintained at $350 \pm 2°$ C.

Anhydrous calcium sulfate or Drierite was used as the water-absorbent, both in the inlet hydrogen drying tube F and in the absorption tubes N. The use of this drying agent is particularly advantageous in the analysis of compounds containing nitrogen and sulfur because it does not absorb ammonia or hydrogen sulphide.

PROCEDURE

The procedure followed in analyzing samples of rubber is essentially the same as that described by Russell and Fulton[9] and Marks[11]. The use of Raney nickel, which is already in the elementary state, makes it unnecessary to reduce the catalyst. However, it is advisable to pass hydrogen through the freshly-loaded system for several hours with the middle furnace at 900° C. and the reduction unit at 400° C. to establish the minimum blank. The temperature of the reduction unit is then lowered to 350° C., the temperature used in making a determination.

The weighed absorption tubes are connected and the sample in the quartz boat is introduced into the tube with the volatilization unit cold; the flow of hydrogen is increased until it escapes through the emergency release. The flow is then decreased to 75 to 90 cc. per minute. In general, it is advisable to pass the hydrogen through the system as rapidly as possible, thereby decreasing the amount of carbon deposited on the cracking surface, and still avoiding incomplete cracking of the sample. The latter condition is indicated by an odor of gasoline-like hydrocarbons at the end of the absorption tubes. The sample is volatilized over a thirty-minute period, by raising the temperature of the first unit gradually to 875° C. The hydrogen flow is continued for another thirty minutes to sweep out the system thoroughly before the absorption tubes are weighed (the second tube need not be weighed, except when the first tube has been in use for some time). After each analysis a thirty-minute blank test is run. Whenever the system is run overnight, the first analysis is always low. The explanation for this observation is not definitely known, but it is postulated that it may be due to an equilibrium set up between nickel, water and their reaction products, as:

$$Ni + H_2O \rightleftarrows NiO + H_2.$$

After approximately ten determinations have been made, the cracking surface becomes choked with carbon, as indicated by the appearance of incompletely cracked oily products in the exit end of the tube. Air is then drawn through the tube, which is heated to 700° to 900° C., to burn out the carbon. The catalysts are

removed, the nickel discarded, and the platinum reactivated by heating it to redness in a casserole for 6 hours. Raney nickel is usually stored as a slurry in 95% ethyl alcohol. When the tube is loaded, it is first filled to a height of 10 inches with this slurry, placed in the furnace, and the alcohol volatilized by gentle heating in a stream of hydrogen. The reactivated platinum on quartz is then added, while the flow of hydrogen is continued.

CATALYSTS

The adaptability of the Raney nickel catalyst to the requirements of this method was checked by comparing its activity with that of the catalyst described by Russell and Fulton[9] in the analysis of such reference compounds as carefully purified succinic acid and benzophenone. The results obtained, together with descriptions of the catalyst preparations, are presented in Table I.

TABLE I

COMPARISON OF CATALYSTS

Catalyst	Description	Oxygen found, % Benzophenone Calc. = 8.79	Oxygen found, % Succinic acid Calc. = 54.21
I–S	Raney nickel 50, plus kieselguhr 50.....	8.82	53.84
		8.76	54.38
		8.67	54.35
II–S	Same as I–S, but containing 2% ThO_2 on the nickel.	—	53.91
		—	54.23
		—	53.76
III–S	Raney nickel, plus 2% ThO_2 No kieselguhr.	—	54.16
		—	54.07
		—	53.83
III–O	Same as III–S but by a different analyst	8.98	—
		8.60	—
		8.42	—
IV–S	Nickel by reduction of Nio + 2% ThO_2.	—	52.08
		—	53.90
		—	54.02

All of the Raney nickel catalyst proved as effective as the one derived from nickel oxide. Catalyst III was adopted for the latter part of the work because of its greater resistance to sulfur poisoning. Goodloe and Frazer[16] have reported recently that a reduced nickel chromite catalyst is particularly resistant to sulfur poisoning and have used it in applying the ter Meulen method to sulfur compounds. The applicability of this catalyst to the analysis of rubber stocks is now being checked in this laboratory.

The platinized quartz catalyst was prepared according to the procedure of Russell and Fulton[9]. The preparation of the palladized asbestos used in the hydrogen preheater followed the procedure of Paal and Karl[17].

ANALYSIS OF VARIOUS RUBBERS FOR OXYGEN CONTENT

The method was applied first to the determination of the oxygen content of two commercial raw rubbers and of rubber hydrocarbon purified by the fractional precipitation method of Midgley, Henne and Renoll[18]. The results of all three determinations are presented in Table II.

While the figure found for the oxygen content of the purified rubber agrees well with that obtained by Midgley, Henne, Shepard and Renoll[3], it is believed that the

figure is of little significance because the accuracy of the method attained in this work is certainly no greater than 0.1%.

TABLE II

OXYGEN CONTENT OF VARIOUS RUBBERS *

Description	Weight of water,† g.	Oxygen, %
No. 1 Smoked sheet	0.0162	1.42
	0.0145	1.29
	0.0144	1.28
	0.0152	1.35
	Average	1.33
No. 1 Smoked sheet dried *in vacuo* one week	0.0144	1.28
	0.0136	1.21
	0.0160	1.42
	Average	1.30
No. 1 Pale crepe	0.141	1.25
	0.152	1.34
	Average	1.29
Rubber hydrocarbon by fractional precipitation, Midgley.	0.0011	0.10
	0.0007	0.06
	Average	0.08

* Nickel catalyst—No. I-S. † Sample weight in all determinations = 1.0000 g.

EFFECT OF MILLING ON OXYGEN CONTENT

Pale crepe was broken down on a cold 12-inch experimental mill and samples were taken at 15-minute intervals. On analysis, these samples gave the results presented in Table III. Although the figures found for oxygen gain are open to the criticism offered immediately above, the total increase is of sufficient magnitude to be submitted as direct evidence in support of the conclusion of Cotton[19] and Busse[20] that oxidation is an essential factor in mastication.

TABLE III

OXYGEN GAIN DURING MILLING *

Milling time	Oxygen present, %	Oxygen gain, %
0 minutes	1.29	—
15 "	1.36	0.07
30 "	1.41	0.12
45 "	1.40	0.11
60 "	1.46	0.17

* Nickel catalyst—No. III-O.

INCREASE IN OXYGEN CONTENT DURING GEER-OVEN AND OXYGEN-BOMB AGING

The method was applied to compounded stocks in the study of the extent of the oxidation occurring in Geer-oven and oxygen-bomb aging. Because the experimental conditions are so different in these tests, it would be expected that the increase in the percentage of combined oxygen found in the same stock aged by the two methods would vary. The former test, involving the heating of the sample in circulating air, allows for the escape of volatile oxidation products. In the latter, since the operation is carried out at a greatly increased pressure and concentration of oxygen in a static condition, the oxidation reaction is predominant and the

resulting products are more firmly held in the sample. However, no data comparing the oxygen contents of rubbers aged by the two methods have been reported.

To check this point experimentally, the same vulcanized stock was aged by both procedures and the gain in weight and increase in combined oxygen were measured.

The original stock studied, chosen because of its lower sulfur content and hence smaller poisoning effect on the catalysts, proved to be too age-resistant. Accordingly, 0.3% of copper oleate was added to catalyze the oxidation. Both stocks are shown in Table IV, together with their calculated oxygen contents.

Table IV

Stocks Used in Oven *vs.* Bomb Study and Calculated Oxygen Contents

	Formulae Parts by weight No. 1	No. 2	Oxygen content of ingredient
Smoked sheet	100	100	1.33
Zinc oxide	5	5	0.984
Stearic acid	2	2	0.225
Sulfur	1	1	—
Benzothiazyl disulfide	1	1	—
Tetramethylthiuram disulfide	0.25	0.25	—
Copper oleate	—	0.30	0.03
Calculated oxygen (%)	2.32	2.36	—

Table V

Analysis of Vulcanized Stocks *

Sample	Weight of water,† g.	Oxygen, %
Stock No. 1	0.0254	2.26
	0.0280	2.48
	0.0262	2.33
	Average	2.36
Stock No. 2	0.0244	2.17
	0.0274	2.43
	0.0282	2.51
	Average	2.37

* Nickel catalyst—No. I-S.
† Sample weight in all determinations = 1.000 g.

These stocks were vulcanized at 127° C. for 40 minutes, the optimum time. Dumb-bell specimens cut from the vulcanized sheets were allowed to come to equilibrium with atmospheric moisture and were then weighed. After aging, the gain in weight was determined by reweighing the specimens under the same conditions. The samples used in the oxygen determination were taken from the constricted portion of the dumb-bell specimen. For the stocks used, it may be assumed that all the oxygen absorbed during aging combined with the rubber or its "resins." The values for combined oxygen and increase in weight are therefore calculated on the basis of the rubber present and not on the total weight of the stock.

The results obtained in the determination of oxygen in the unaged stocks agree well with the calculated values, and are presented in Table V. They show that the method is applicable to vulcanized rubber containing appreciable quantities of sulfur.

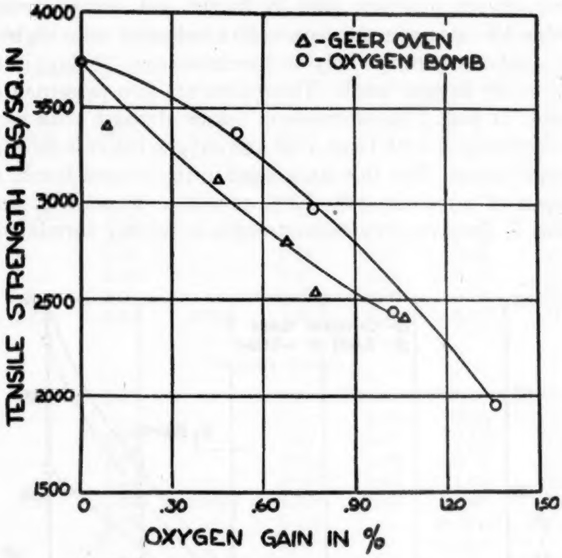

FIG. 2.—Gain in oxygen *vs.* decrease in tensile strength. Benzothiazyl disulfide stock plus copper oleate.

FIG. 3.—Correlation of oxygen gain with decrease in tensile strength for benzothiazyl disulfide stock. Effect of copper oleate.

The data for oxygen analyses, gain in weight and tensile strength are summarized in Table VI. Because the tensile data indicated only slight deterioration of stock No. 1, analyses were run only on specimens aged 35 days in the Geer oven and 120 hours in the oxygen bomb. These data are also presented graphically in Figs. 2, 3, and 4. In Fig. 2 the decrease in tensile strength with increase in combined oxygen occurring in both Geer oven and oxygen bomb is shown for the stock containing copper oleate. For this stock aged in the oxygen bomb, an increase in combined oxygen of approximately 1.3% caused a decrease in tensile strength of 50%. In Fig. 3, the drop in tensile strength is further correlated with gain in

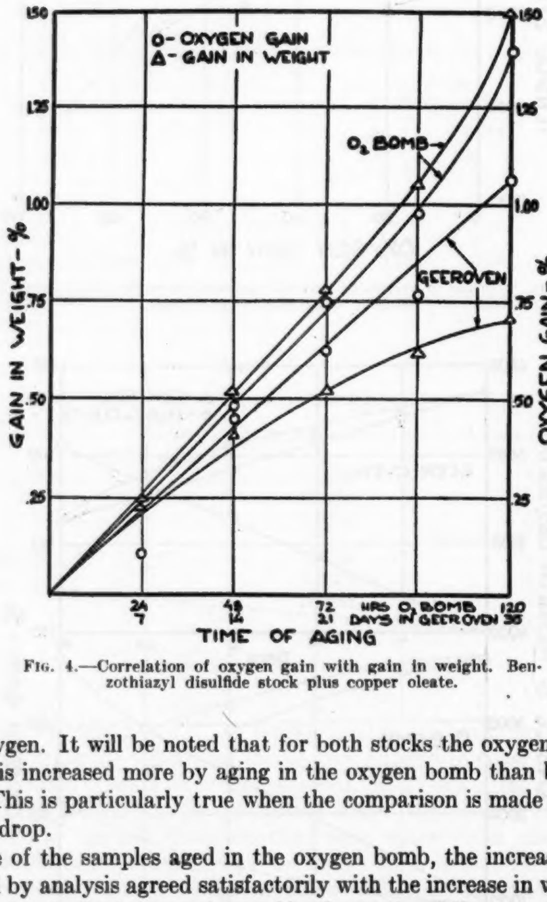

FIG. 4.—Correlation of oxygen gain with gain in weight. Benzothiazyl disulfide stock plus copper oleate.

combined oxygen. It will be noted that for both stocks the oxygen content, as to be expected, is increased more by aging in the oxygen bomb than by aging in the Geer oven. This is particularly true when the comparison is made on the basis of equal tensile drop.

In the case of the samples aged in the oxygen bomb, the increase in combined oxygen found by analysis agreed satisfactorily with the increase in weight (Fig. 4). On the other hand, the increase in combined oxygen of the samples aged in the Geer oven exceeded the gain in weight appreciably. These results indicate that the changes taking place in the rubber during aging by the two methods are distinctly different. Although the fundamental reaction in both cases is one of oxidation, aging in the Geer oven involves in addition thermal decomposition followed by volatilization of oxidation products of the rubber or other ingredients.

TABLE VI

SUMMARY OF DATA COMPARING GEER OVEN AND OXYGEN BOMB AGING *

Time of aging	Oxygen by analysis, % † Stock No. 1	Oxygen by analysis, % † Stock No. 2	Oxygen gain, % † Stock No. 1	Oxygen gain, % † Stock No. 2	Gain in weight, % † Stock No. 1	Gain in weight, % † Stock No. 2	Tensile strength, lbs. per sq. inch Stock No. 1	Tensile strength, lbs. per sq. inch Stock No. 2
Geer Oven								
0 days	2.36	2.37	—	—	—	—	3740	3740
7 "	—	2.46	—	0.10	0.15	0.25	3400	3380
14 "	—	2.79	—	0.46	0.19	0.40	3330	3160
21 "	—	2.98	—	0.67	0.26	0.53	3170	2800
28 "	—	3.03	—	0.72	0.30	0.64	2780	2510
35 "	2.63	3.34	0.29	1.06	0.40	0.71	2340	2400
Oxygen Bomb								
0 hrs.	2.36	2.37	—	—	—	—	3740	3740
24 "	—	—	—	—	0.18	0.23	3675	—
48 "	—	2.82	—	0.49	0.26	0.53	3500	3300
72 "	—	3.06	—	0.65	0.34	0.78	3150	2930
96 "	—	3.26	—	0.98	0.43	1.05	2860	2400
120 "	2.92	3.64	0.60	1.39	0.48	1.46	2660	1950
144 "	—	7.83	—	6.10	—	melted	—	melted
168 "	—	10.00	—	8.35	—	melted	—	melted

* Nickel catalyst—No. I-S.
† Percentage is calculated on the rubber.

EFFECT OF ANTIOXIDANTS ON THE INCREASE IN COMBINED OXYGEN DURING AGING

The effect on the rate of deterioration in tensile strength of vulcanized rubber during aging in the oxygen bomb is used extensively as the measure of the efficiency of antioxidants. However, the effect of antioxidants on the state of oxidation of rubber aged in the oxygen bomb has not been known. The application of the ter Meulen method in this work to the analysis of stocks aged in the oxygen bomb has given this information.

The antioxidants used, together with their physical constants, are given in Table VII. The first three were obtained in a high state of purity by recrystallization of the commercial products. The fourth, 5,5-dimethylacridane, was isolated by twice fractionally distilling in a vacuum the acetonediphenylamine condensation product known as BLE. The distillation product was recrystallized from methanol to give a final yield of 6%.

The use of the combination of benzothiazyl disulfide and tetramethylthiuram disulfide accelerators (see above) gave stocks which, although no antioxidant was present, were very resistant to aging. In the study of antioxidants, the protection

TABLE VII

ANTIOXIDANTS STUDIED

Name	Physical constants
Phenyl-β-naphthylamine	m.p. 107° C.
p-Hydroxy-N-phenylmorpholine	m.p. 168–9° C.
6-Phenyl-2,2,4-trimethyl-1,2,-dihydroquinoline .	m.p. 101–2° C.
5,5-Dimethylacridane	b.p. 140–5° C./3–5 mm. m.p. 123–4° C.

afforded by the accelerator should be kept at a minimum. Accordingly, diphenylguanidine, which gives rapidly aging vulcanizates, was substituted for the accelerator combination just mentioned. The control and stocks containing antioxidants, together with their calculated oxygen contents, are given in Table VIII. In order to minimize sulfur-poisoning of the catalysts, the amount of sulfur used was below that usually considered to be good practice for diphenylguanidine acceleration. To compensate for this loss of vulcanizing power, the amount of accelerator used was increased by 50%.

These stocks were vulcanized at 142° C. for 60 minutes (optimum). Dumb-bell specimens cut from the vulcanized sheets were aged in the oxygen bomb, stock No. 3 for 24 and 48 hours, the others for 24, 48, 72 and 96 hours. Each stock was aged individually in order to prevent migration of antioxidant from one stock to another. At the end of 24 hours the specimens of the control stock had not lost their shape, but the tensile strength had decreased to the point where it could not be read on the Scott machine. At the end of 48 hours this stock had deteriorated

Table VIII

Stocks Used in Antioxidant Study

	Parts by weight				
	No. 3	No. 4	No. 5	No. 6	No. 7
Pale crepe	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Sulfur	2	2	2	2	2
Diphenylguanidine	1.5	1.5	1.5	1.5	1.5
5,5-Dimethylacridane	—	1	—	—	—
p-Hydroxy-*N*-phenylmorpholine	—	—	1	—	—
6-Phenyl-2,2,4-trimethyl-1,2-dihydroquinoline	—	—	—	1	—
Phenyl-β-naphthylamine	—	—	—	—	1
Calculated oxygen (%)	2.26	2.24	2.40	2.24	2.24

to a semiplastic mass. The antioxidant stocks still possessed fair tensile strength after 96 hours' aging.

The progress of the deterioration of the four stocks containing antioxidants was followed by analyses for combined oxygen and by the measurement of tensile strength. The results are summarized in Table IX and analyzed graphically in Figs. 5 and 6. The curves in Fig. 5 show the expected correlation between the effectiveness of an antioxidant in retarding oxygen absorption and its ability to maintain tensile strength during aging—in general, the lower the oxygen absorption, the greater the resistance to deterioration of physical properties. Of the four antioxidants studied, phenyl-β-naphthylamine affords the greatest protection against oxidation. *p*-Hydroxy-*N*-phenylmorpholine and 6-phenyl-2,2,4-trimethyl-1-2-dihydroquinoline occupy an intermediate position, with 5,5-dimethylacridane giving the poorest retardation. Comparison with the control, however, shows that all are relatively efficient antioxidants.

For all the antioxidants it may be said that as the aging proceeds, the ability of the antioxidant to retard oxidation diminishes.

The results indicate (Fig. 6) that the relationship of increase in oxygen content to decrease in tensile strength is a straight line function during the early stages of aging. With reference to this curve, it should be noted that the spread in points is due to errors in the measurement of tensile strength rather than to the errors involved in the oxygen analysis. The position of the tensile strength values after

24 hours' aging indicated some after-vulcanization during the early stages of aging. Therefore, the left-hand end of the curve was allowed to fall at a point slightly above the 100% tensile strength reference point. As indicated by this curve, an increase in combined oxygen of approximately 1.2% corresponds to a decrease in tensile strength of 50%. Because the control stock was so badly deteriorated in 24 hours, this statement must be restricted to apply only to stocks containing antioxidants. This value of 1.2% combined oxygen compares favorably with those

TABLE IX

SUMMARY OF DATA: EFFECT OF ANTIOXIDANTS ON RELATIONSHIP OF INCREASE IN COMBINED OXYGEN TO DECREASE IN TENSILE STRENGTH

Stock, antioxidant, period of aging	Oxygen* by analysis, %	Increase in combined oxygen, % on the rubber	Tensile strength, lbs. per sq. inch
No. 3. *Control.*			
0 hours	2.32	—	2500
24 "	7.97	6.31	??
48 "	12.14	10.95	melted
No. 4. 5, 5-*Dimethylacridane.*			
0 hours	2.21	—	2400
24 "	2.37	0.18	2180
48 "	2.98	0.85	1450
72 "	3.58	1.52	835
96 "	4.08	2.08	810
No. 5. *p-Hydroxy-N-phenylmorpholine.*			
0 hours	2.28	—	2920
24 "	2.49	0.23	2750
48 "	2.71	0.48	2580
72 "	3.10	0.92	1890
96 "	3.76	1.65	1550
No. 6. 6-*Phenyl*-2,2,4-*trimethyl*-1,2-*dihydroquinoline.*			
0 hours	2.33	—	2600
24 "	2.42	0.10	2600
48 "	2.75	0.47	1900
72 "	3.18	0.95	1410
96 "	3.63	1.45	1250
No. 7. *Phenyl-β-naphthylamine.*			
0 hours	2.21	—	2230
24 "	2.26	0.06	2600
48 "	2.33	0.14	2050
72 "	2.52	0.35	2100
96 "	3.05	0.94	1440

* Nickel catalyst—No. III-O.

obtained by Scheffler[21] for carbon black stocks containing antioxidants. Using a volumetric method similar to that of Marzetti[22] he found that for such stocks accelerated with diphenylguanidine, an oxygen absorption of from 0.9 to 1.2%, depending on the antioxidant present, corresponded to a decrease in tensile strength of 50%. It is significant to note that according to his findings the same stock containing no antioxidant showed an oxygen absorption of only 0.3% to give the same decrease in tensile strength. On the other hand, the value obtained in this work is not in agreement with that found by Kohman[5], who working with a mercaptobenzothiazole-accelerated gum stock observed that the absorption of approximately 0.5% oxygen measured volumetrically resulted in a 50% decrease in tensile strength. The fact that his conditions of aging, 80° C. and 1 atm. of oxygen, differed from those employed in this study may explain this variation. Stock No. 1,

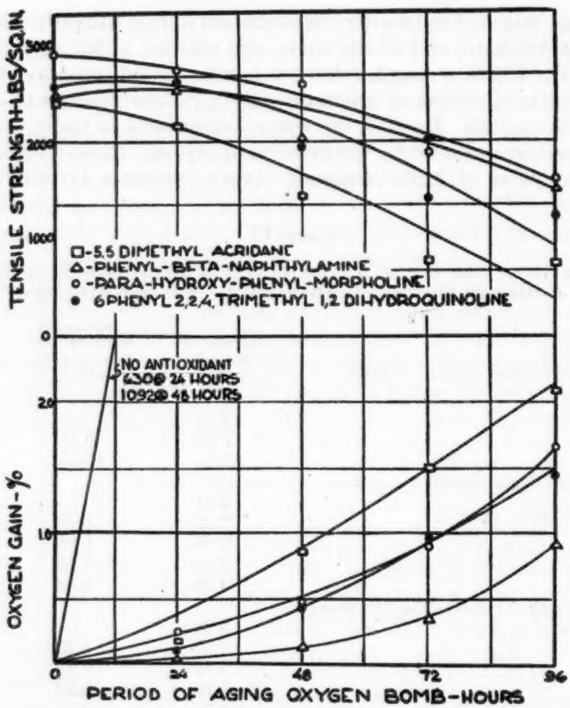

FIG. 5.—Effect of typical antioxidants on oxygen gain and decrease in tensile strength.—D.P.G. stock—oxygen bomb.

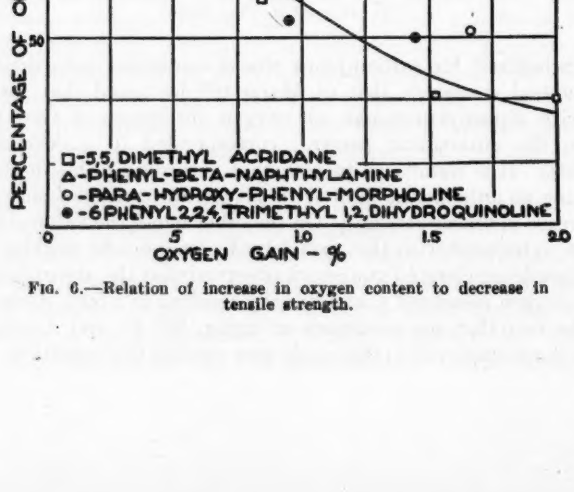

FIG. 6.—Relation of increase in oxygen content to decrease in tensile strength.

herein reported, accelerated with mercaptobenzothiazole plus tetramethylthiuram disulfide, was not aged to the point where its tensile strength had deteriorated 50%. However, by extrapolation of the curves in Figure 3, it is estimated that the increase in combined oxygen corresponding to this drop in tensile strength would be approximately 0.9%. The same stock plus copper oleate (stock No. 2) required an increase in combined oxygen of 1.35% to give a 50% decrease in tensile strength. The amount of oxygen which might react with the small amount of copper oleate present is far too small to explain this difference. The fact that the increase in combined oxygen corresponding to a given decrease in tensile strength was greater for this stock than for those containing antioxidants indicates that the combination of accelerators used, benzothiazyl disulfide plus tetramethylthiuram disulfide, may possess a specific action of its own to give tolerance against increased amounts of combined oxygen. This may not be concluded definitely, however, because the effect may have been due in part to the smaller amount of sulfur present in this stock.

ADDITIONAL APPLICATIONS OF THE METHOD

The direct determination of oxygen in rubber should find application in many fields of rubber research. The work reported herein represents only a beginning in this approach to the problem of aging. The method should be of value in studying the oxygen content of carbon black and the general problem of the effect of this oxygen on rubber. Work is now in progress in this laboratory on applying the method to the study of vulcanization by oxidizing agents such as di- and trinitrobenzenes and benzoyl peroxide, whereby it is hoped that some information may be gained on the question of whether such vulcanization involves chemical combination with oxygen or polymerization through dehydrogenation.

SUMMARY

The ter Meulen method for the direct determination of oxygen has been adapted, with modifications, to the analysis of raw and vulcanized rubbers. Raney nickel has been found to be quite effective as the reducing catalyst and to be satisfactorily resistant to sulfur poisoning.

The method has been applied to the study of the aging of vulcanized rubber in the Geer oven and oxygen bomb. From this study the following conclusions may be drawn:

(1) The increase in combined oxygen is greater in the oxygen bomb than in the Geer oven.

(2) Deterioration of rubber in the oxygen bomb involves oxidation primarily, whereas that occurring in the Geer oven involves not only oxidation but also thermal decomposition followed by volatilization of oxidation products.

(3) The effectiveness of an antioxidant in retarding the absorption of oxygen in oxygen-bomb aging agrees well with its ability to maintain the physical properties of the stock in which it is present.

(4) The deterioration in physical properties of a rubber stock in the oxygen bomb during the early stages of aging is a linear function of the increase in combined oxygen. For stocks containing antioxidants and diphenylguanidine as the accelerator, an increase in combined oxygen of approximately 1.2% corresponds to a decrease in tensile strength of 50%.

(5) The relationship of increase in combined oxygen to decrease in tensile strength seems to be affected not only by antioxidants, but also by accelerators of vulcanization.

A slight but definite increase in combined oxygen was found to occur during plasticization of rubber by milling.

ACKNOWLEDGMENT

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AN ACCELERATED AGING TEST AT ROOM TEMPERATURE *

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Accelerated aging in an oven, heated to a more or less elevated temperature, is one of the most valuable tests at the disposal of the rubber technologist for examining the behavior of different compounds in practical use.

Geer in 1916 described a now well-established oven test at 160° F., he and Evans giving more details in 1921. In this latter paper they stated in particular that with proper use of their test, one day in the oven could be taken as equal to six months of natural life.

Other attempts to foretell more exactly the natural life of rubber from accelerated aging data have proved useless. The figures obtained for life at different temperatures are not always in the same ratio, so that calculation of the corresponding times at room temperature depends on the temperature used in the heat test. This has been shown in experimental work of many authors, particularly Williams and Neal, Milligan and Shaw, Bierer and Davis, and Somerville and Russell. The matter has been thoroughly discussed in a "Symposium on Aging" presented before the New York Rubber Group of the American Chemical Society in 1929.

The writer, in unpublished work carried out some years ago, tested the aging of many typical compounds at four temperatures, ranging from 57° to 98° C. The behavior of these compounds at different temperatures was very different. For example, a gas black compound aged much more rapidly than a "pure gum" at high temperatures, while at lower temperatures the reverse was probably true. Again, a smoked sheet stock containing an accelerator was superior at the higher temperatures to a non-accelerated stock of sprayed rubber, but at the lower temperatures the latter had much the advantage.

An attempt to establish an exponential formula with two constants to represent the life of rubber at different temperatures was quite successful in the range of temperature explored, but on extrapolating to room temperature in a case of very rapid aging which could be checked experimentally, the calculated value was more than double the actual life.

It is true that in some uses of rubber, even among the most important, the rubber attains temperatures equal to or higher than those of the oven tests. In such cases the accelerated aging test is not artificial, but may be considered a service test. Many other rubber articles, however, are used more or less exclusively at room temperature. For these, and for the former articles during storage and rest, aging at room temperature remains all-important.

Stevens first studied natural aging, in a paper in the *Journal of the Society of Chemical Industry* in 1916. In this and in subsequent papers, he collected many data showing a clear relation between the rate of aging of a "pure gum" (rubber 90, sulfur 10) and its vulcanization coefficient.

The subsequent introduction of accelerators and antioxidants has made it difficult to apply Stevens' method, owing to the great increase in the life of

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rubber realized by the application of these materials. While "pure gum" compounds perish in a few years, accelerated stocks require a much longer time, all the more when antioxidants are present also. So that while natural life testing remains very important as a special control of durability, it can never serve as a routine test.

When antioxidants were introduced the writer attempted to obtain a room-temperature aging test fast enough to provide practical results in a reasonable period of time. This was made necessary by the doubt whether these newly proposed and costly materials, not then tested over long periods of natural life, would behave differently in oven tests and at room temperature. If for nothing more than to make a selection among the numerous products on the market, it was very important as a control on oven-test to have a non-artificial test, or at least a test that was artificial in another way. To this end the writer had recourse to the well-known rapid aging of low-grade rubber.

Aging was tested mechanically on samples 4 mm. thick, cut in the form of Schopper rings, the stress-strain curve being obtained on a rotating-pulley machine of the Schopper type.

On the basis of preliminary tests, Massai rubber was selected as a fast-perishing grade, since it was similar to *Hevea* as regards the tensile properties of the new rubber and so well-fitted for mechanical testing.

Massai rubber was mixed with 10% of sulfur and vulcanized for 230 minutes at 143° C. When tested one day after vulcanization, the tensile product was 7.2 kg. per sq. mm., with a modulus of 135 g. per sq. mm. at 300% elongation. Samples exposed in air in an ordinary room, in diffused light at an average temperature of 20° C., perished in 4 weeks, the tensile product being reduced to 1.8 kg. per sq. mm.

Several antioxidants were compounded separately in the same base stock, using 1% on the rubber. Some accelerators were used also to see if their enhancing effects were likely to give results similar to those of antioxidants. The rates of vulcanization differed considerably in these stocks, the more so for the accelerated stocks, although these did not contain zinc oxide.

The question arose, therefore, how to vulcanize these mixtures for comparison of their durability, aging being closely connected with degree of vulcanization. As in previous early work, the writer preferred to compare the different compounds at the same mechanical degree of vulcanization. The modulus at 300% elongation was taken as a measure of vulcanization, the value of 135 g. per sq. mm. being fixed upon, as in the preliminary tests on the base stock. This value corresponded to a vulcanization a little lower than the optimum. Numerous equally vulcanized samples were prepared and suspended on strings in air in diffused daylight at an average temperature of 24° C.

Mechanical tests were done on samples taken weekly, or at longer intervals when previous tests indicated need to extend the time. Accidental low breaking figures were disregarded. Changes in the tensile product were graphed, and each compound was considered to have perished when the tensile product fell to 5 kg. per sq. mm., the "life" of the rubber being taken as the period of time for this to occur.

The following table indicates the vulcanizing conditions and life of each compound examined.

Such results, and others not reported here because scarcely interesting to-day, served to confirm the real effectiveness of antioxidants. They confirmed also the good antiaging properties of some accelerators, indicating that antioxidants need not be used in articles of less importance.

This aging method has been used again recently to test some new antioxidants. Massai rubber not being available on this occasion, the writer had recourse to acetone-extracted *Hevea* rubber, it being well-known that extraction of the natural antioxidants from rubber promotes its rapid aging. This material has the advantage also of being, if not absolutely standard, less variable than a low-grade rubber. Its rate of aging, also, may be greater than that of low-grade rubber.

Preliminary tests led to the selection of a re-milled crepe, and later of a fine pale first-latex crepe. Tests with the latter are still in progress. The rubber was acetone-extracted by immersing it in the cold in a large quantity of acetone. Immersion lasted 5 days, during which time the liquid was renewed 4 times. Extraction could have been made in a Soxhlet apparatus.

TABLE I

Ingredient, 1% on rubber	Vulc., 143° C., mins.	Life, days
None (base stock)	230	12
2, 4-Diaminodiphenylamine	55	64
Acetaldehydeaniline (acid-condensed)	85	91
Aldol-α-naphthylamine	170	217
Phenyl-α-naphthylamine	260	182
Indanylresorcinol	230	94
Diphenylguanidine	80	77
Mercaptobenzothiazole	72	43
Butyraldehydeaniline	46	108
Formaldehydeethylamine	24	257
Heptaldehydeaniline	13	211

TABLE II

Ingredient	Proportion, %	Life, days
None (base stock)	0	10
Rosin	3	1
Pine tar	3	55
Stearic acid	3	5
Paraffin	3	8
Phenyl-β-naphthylamine	1	>153
p-Hydroxydiphenylamine	1	>153
Heptaldehydeaniline	1	>153

The extracted remilled and first-latex crepes, compounded with 7% of sulfur and vulcanized to a modulus of 100 g. per sq. mm. at 300% elongation, perished at room temperature in 10 and 12 days, respectively.

In one set of tests, the behavior of the remilled crepe stock, with 7% of sulfur, was examined after compounding with the materials indicated in Table II.

As the preparation of the numerous samples occupied rather a long period of time, and the rate of aging of some of them was very great at room temperature, all samples were stored in an atmosphere of carbon dioxide to preserve them from oxidation until age-exposure was begun simultaneously on them all.

The results confirm the well-known proöxygen action of rosin, and the slight antioxygen action of pine tar. Stearic acid and paraffin seem to shorten the life of the rubber. This slight action may be due to their plasticizing effect in lowering the modulus, thus requiring a longer vulcanization period to attain the predetermined modulus adopted for all the new rubbers. It is of interest to note that under the test conditions described, light must have a negligible action, otherwise the paraffin should have prolonged the life of the compound.

The three rubbers containing 1% of antioxidant or accelerator did not undergo any perishing in 153 days, after which the tests were interrupted due to exhaustion of test rings.

There were frequent accidental low tensile results in these tests, the vulcanization being probably too near to the optimum. Therefore, in the second set of tests, using first-latex crepe, it has been preferred to lower the modulus, adopting the value of 160 g. per sq. mm. at 500% elongation. To expedite the results, the concentration of antioxidant was reduced to 0.1%, and in this concentration there has been no decay of the rubber in 5 months in the presence of phenyl-β-naphthylamine or *p*-hydroxydiphenylamine, while another sample containing the reaction product of acetone and diphenylamine lasted 84 days.

An odd result in these later tests is that, in the presence of magnesium oxide, rosin prolongs the life of the rubber and pine tar shortens it.

Naturally these results ought to be confirmed by a number of repeat tests. It may be observed, also, that to give a well-defined value to these room-temperature aging data, it will be advisable to expose the samples in a conditioned room, analogous to rooms used for the mechanical testing of textiles.

A RELATIONSHIP BETWEEN THE CRITICAL OXIDATION POTENTIALS AND ANTIOXIDANT ACTIVITIES OF RUBBER ANTIOXIDANTS *

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INTRODUCTION

Fieser[1] and his coworkers have extended the work of Conant[2] and his collaborators on the measurement of the oxidation-reduction potentials of irreversible systems. They were able to measure a characteristic potential of the irreversible oxidation-reduction system which was independent of the rate at which the reaction occurred. The potential thus determined for various systems was termed the critical oxidation potential, E_c, of the system. It was defined as that potential at which the rate of the oxidation reaction becomes so small as to be just detectable with the technique employed. Fieser[3] and his coworkers have shown also that E_c is definitely related to the normal oxidation-reduction potential, E_o, by the relationship $E_c = E_o - 0.068\text{v}$.

Gershinowitz[4] has recently presented a thermodynamic explanation for Conant's observation that a definite relationship exists between the rate of an irreversible oxidation-reduction reaction and the oxidation-reduction potentials of the reagents used.

Egloff and Lowry[5] have correlated the values E_c with the inhibiting effects of various compounds on gum formation in gasoline. This correlation indicated that an optimum value of E_c for gum inhibitors exists between 0.6 and 0.8 volt. While there is in general no direct relationship between the compounds which are good inhibitors of gum formation for petroleum, and those with marked antioxidant activity in rubber, a similar optimum range of ease of oxidizability would be expected.

Recently, Elley[6] has related the "apparent oxidation potential" of several compounds to their antioxidant activity in rubber. The results, plotted graphically, indicate a definite relationship between the two properties, with the maximum antioxidant activity between 0.6 vol. and 0.95 volt.

EXPERIMENTAL PART

The technique employed in determining the E_c value of each substance was that described by Fieser[3]. The procedure and precautions recommended by him were observed.

The compounds tested were either carefully purified commercial samples or pure materials synthesized in the laboratory. The melting-point ranges for the substances studied are given in column 2 of Table I. The reference systems used to determine E_c are designated in column 3 of the Table, according to Fieser's code[3].

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The critical oxidation potentials recorded are the values obtained from duplicate determinations on the same sample. Determinations of E_c were made for diphenylamine, *p*-aminophenol and β-naphthol, and values were obtained which agreed within one millivolt with those reported by Fieser.

The substances were each compounded in the following formula to be tested for antioxidant activity.

Rubber (smoked sheet)	100
Sulfur	3
Zinc oxide	3
Channel black (rubber grade)	50
Stearic acid	3
Pine tar	3
Mercaptobenzothiazole	1
Antioxidant	1
	164

TABLE I

Name	Melting point (° C.)	System	E_c (v.)	Tensile strength (lbs. per sq. in.)
Di-*o*-tolylamine	(b.p. 140 to 145° C. at 2 mm.)	Fe	0.88	3000 ± 200
Di-*p*-tolylamine	79–80	Fe	0.864	3500
4-Ethoxydiphenylamine	71–72	Fe	0.846	3600
4-Isopropoxydiphenylamine	86–87	Fe	0.863	3800
p,p'-Dimethoxydiphenylamine	96–97	Fe	0.797	3600
2,4-Diaminodiphenylamine	130–131	Fe	0.54	3000
N,N'-Diphenyl-*p*-phenylenediamine	145–146	Fe	0.67	3900
N,N'-Di-*p*-tolyl-*p*-phenylenediamine	179–180	Fe	0.68	3800
Diphenylethylenediamine	63–64.5	Fe	0.875	3100
Phenyl-β-naphthylamine	108–109	Fe	0.823	3300
p-Ethylphenyl-β-naphthylamine	63–64	Fe	0.836	3500
p-Ethoxyphenyl-β-naphthylamine	86–87	Fe	0.760	3600
5,5-Dimethylacridane	121–2	Fe	0.852	3800
5,5,10-Trimethylacridane	100–100.5	Fe	0.895	2300
2,2,4-Trimethyl-1,2-dihydroquinoline	25–26	Fe	0.829	3300
2,2,4-Trimethyl-6-pheny-1,2-dihydroquinoline	102–102.5	Fe	0.863	3800
Carbazole	239–240	Mo	1.14	1500
α-Naphthol	94 (lit.)	Fe	0.792	2300
4-Cyano-1-amino-2-naphthol	205–206	B	0.5	2800
4-Hydroxytriphenylcarbinol	156–157	Mo	1.1	2100
p-Hydroxy-*N*-phenylmorpholine	171–172	Fe	0.765	2400
Diamylhydroquinone	183–184	Fe	0.713	2900
Thioglycollic acid (Eastman Kodak) (pract.)	(b.p. 104 to 106° C. at 11 mm.)	B	0.5	2800
N,N'-Diphenylpiperazine	164–165	Fe	0.88	2300
p-Tolunitrile	29–29.5	Fe	0.9	2800
4,4'-(Dimethyldiamino)diphenylmethane	—	Mo	0.99	3100

Stocks were vulcanized for 60, 90 and 120 minutes at 274° F. (133° C.), in slabs 0.125 inch thick. The 0.25-inch dumb-bell test strips cut from these slabs were aged in the Bierer-Davis oxygen bomb under 300 lb. per sq. in. pressure at 70° C. for 46 hours.

The criterion chosen for judging the antioxidant activity of a compound was the optimum tensile strength of the aged stock into which the compound had been incorporated.

The control stock without antioxidant had optimum tensile strengths, unaged, of 4500 lb. per sq. in., and aged, 1800 lb. per sq. in. These optimum tensile values are reported as ± 200 lb. per sq. in., since the experimental error of the tensile test is of that order.

The materials recorded in Table I are those for which the values of E_c were determined. The values of E_c for the compounds in Table II were obtained from Fieser's data[8]. The antioxidant activities of the compounds are reported as tensile strengths.

In Figure 1 the tensile values in lbs. per sq. in. are plotted as ordinates. They are represented as lines 400 lbs. per sq. in. in length, to agree with the experi-

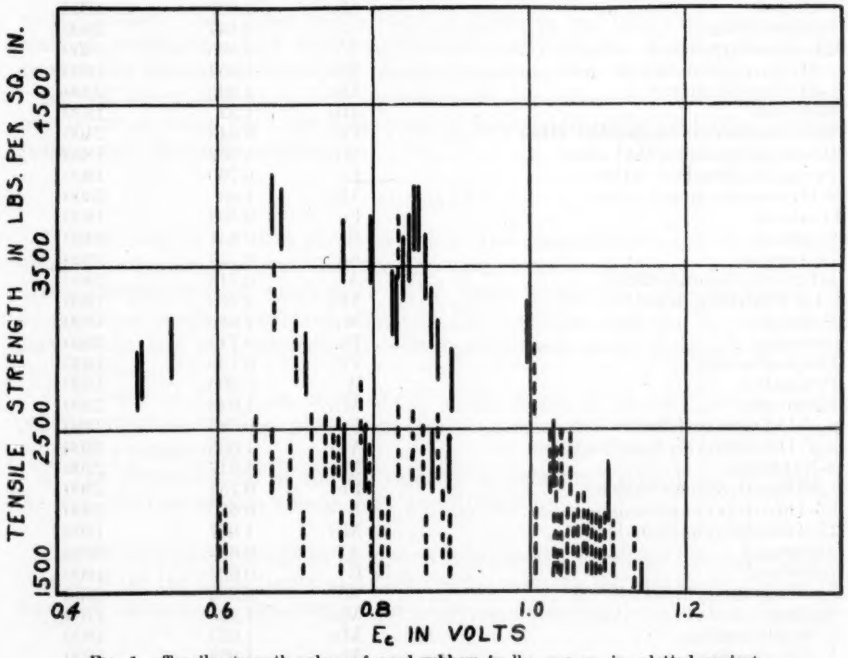

FIG. 1.—Tensile strength values of aged rubbers in lbs. per sq. in. plotted against E_c values, in volts, of the antioxidants tested.

mental error of the tensile test. The abscissæ are the values of E_c in volts. Those compounds for which E_c was determined are represented by solid lines, and those for which E_c was obtained from Fieser's data, by broken lines.

DISCUSSION

It is evident from Figure 1 that a general relationship exists between E_c and antioxidant activity. Those compounds which exhibit antioxidant activity lie in a range of E_c values approximately between 0.5 volt and 1.0 volt. The very effective antioxidants have E_c values between 0.65 volt and 0.90 volt. The converse of this statement, that all compounds which have an E_c value within this optimum range exhibit marked antioxidant activity, is not correct, however. This observation is not in agreement with that of Elley[6]. He has shown that a definite relationship exists between an "apparent oxidation potential" and the relative effectiveness of rubber antioxidants. The maximum activity, according

to Elley, occurs for those compounds whose potentials lie between 0.6 volt and 1.00 volt.

The reaction between rubber and oxygen probably occurs according to some specific oxidation mechanism. Also, the effectiveness of a compound as an

TABLE II

Name	System	E_c (v.)	Tensile strength (lbs. per sq. in.)
Phenol	Mo	1.089	1800
o-Cresol	Mo	1.040	1800
m-Cresol	Mo	1.080	1800
p-Cresol	Mo	1.089	1800
Hydroquinone	—	0.647	2800
2,4-Dimethylphenol	W	0.895	1800
p-Hydroxyphenylacetic acid	Mo	1.051	1800
p-Hydroxydiphenyl	Mo	1.036	2200
Saligenin	Mo	1.52	1800
Hydroquinonemonomethyl ether	Fe	0.848	2400
Resorcinolmonomethyl ether	Mo	1.052	1800
Pyrogalloldimethyl ether	Fe	0.760	1800
p-Hydroxydiphenyl ether	Mo	1.03	2300
Guaiacol	Fe	0.868	1800
Eugenol	Fe	0.831	2400
Isoeugenol	Fe	0.757	2300
p-Dimethylaminophenol	A	0.718	2400
2,4,6-Trichlorophenol	Mo	1.103	1800
Vanillin	Mo	1.080	1800
Catechol	Fe	0.742	2300
Phloroglucinol	Fe	0.799	1800
Pyrogallol	B	0.609	1800
Resorcinol	Mo	1.043	2300
p,p'-Dihydroxystilbene	Fe	0.786	2100
p,p'-Dihydroxydiphenylmethane	Mo	1.038	1800
β-Naphthol	Mo	1.017	2200
1,3-Dihydroxynaphthalene	Fe	0.754	2300
1,5-Dihydroxynaphthalene	A	0.673	2300
2,7-Dihydroxynaphthalene	Mo	1.007	1800
Anthranol	A	0.693	2200
α-Anthrol	B	0.602	1900
p,p'-Dihydroxydiphenyl	W	0.882	2400
Aniline	Mo	1.135	1700
N-Methylaniline	Mo	1.053	1800
N-Ethylaniline	Mo	1.038	1800
N-Benzylaniline	Mo	1.057	2200
p-Toluidine	Mo	1.077	1900
Diphenylamine	Mo	1.008	2800
p-Anisidine	W	0.892	1900
m-Toluylenediamine	Fe	0.864	2300
β-Naphthylamine	Mo	1.064	1900
p-Aminophenol	A	0.673	3300
p-Phenylenediamine	A	0.710	1800
p-Aminodiphenylamine	A	0.696	3000
p,p'-Diethoxydiphenylamine	Fe	0.836	3600
n-Propylmercaptan	Fe	0.812	1800
Isopropylmercaptan	Fe	0.819	1900

inhibitor of the reaction would be dependent on the ability of the molecules of the inhibitor to fit into the reaction mechanism and suppress it. Although many substances have E_c values within the optimum range, it does not follow that all of them would have similar oxidation mechanisms or that they could all exhibit effective inhibitor mechanisms to the rubber-oxygen reaction. Several types of compounds have been tested, and only a few of them found with marked anti-

oxidant activity, even though several members of each of the groups tested had E_c values within the optimum range. This fact indicates that a compound must possess some physico-chemical properties other than an E_c value within an optimum range to have marked antioxidant activity.

An explanation is desirable for the presence of an optimum range in the E_c values presented. It was thought that perhaps the E_c for rubber hydrocarbon itself would fall somewhere in the optimum range. Then, those compounds with E_c values above that of rubber would be too difficult to oxidize, and would afford the rubber little protection. Those below E_c for rubber, in value, would gradually decrease in effectiveness as they decrease in E_c because of the increasing affinity for atmospheric oxygen, and the resultant loss in material to afford protection to the rubber. The rubber in the stock is probably not in a very homogeneous state of combination and, under such conditions, oxidation could quite possibly start under several conditions at various potentials.

Several attempts were made to determine E_c for rubber, but no solvent system was found in which both the rubber and a known reversible oxidation-reduction system were mutually soluble.

SUMMARY

1. According to the data presented, all of the compounds tested which exhibit marked antioxidant activity have an E_c value between 0.65 volt and 0.90 volt. Many substances exist which have an E_c value within the optimum range, but do not have much antioxidant activity. The condition that the E_c value for a good antioxidant falls between 0.65 volt and 0.90 volt seems to be necessary but not sufficient.

2. A value of E_c within an optimum range seems to be only one of several possible physico-chemical phenomena which govern the rubber antioxidant activity of a compound.

3. The determination of the E_c value of a compound should not be used as the sole criterion of that compound's antioxidant activity.

The writer wishes to express his appreciation to the Firestone Tire and Rubber Company for the opportunity and facilities for carrying out this work, and to the Research Laboratory personnel for the generous and helpful coöperation extended.

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A PROPOSED NEW METHOD OF RETARDING THE AGING OF VULCANIZED RUBBER BY MEANS OF PEROXIDES AND NITRO COMPOUNDS *

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1. INTRODUCTION

Hitherto only one process has been known for retarding the aging of vulcanized rubber, that is, to apply various reducing agents which inhibit the attack of the oxygen in air and protect the rubber against oxidation, while not interfering with the vulcanization reaction.

However, in recent literature it has been reported that resistance to aging can be increased appreciably by means of low-sulfur vulcanization. This process is not easily put into practice. If a normal sulfur content is present, vulcanization is apt to proceed beyond the required point, and if vulcanization retarders are added to the rubber, incomplete vulcanization may ensue. If vulcanization could be controlled to stop at the primary stage as defined by Blake[1], satisfactory age resistance would be obtained, but control in this manner is almost impossible and the results obtained are not more effective than those given by various well known antioxidants.

The authors have now found that when peroxides and nitrocompounds which act as vulcanizing agents are added to ordinary rubber mixings in the proportion of 0.5 to 1.0% on the rubber, they control the vulcanization reaction and bring about age-resisting effects much superior to that of antioxidants. These reagents act by substituting their vulcanizing effect for part of the sulfur vulcanizing effect. As these agents effect only primary vulcanization and do not give over-vulcanized or hard rubbers, it becomes possible to control the stage at which vulcanization is stopped.

The only doubtful point is that these organic vulcanizing agents are themselves oxidizing agents, so that they may lead to rapid aging on their own account. But it should be noted that whereas they are used in proportions of 4 to 6% for vulcanizing rubber in the present experiments when used as controllers only 0.5 to 1.0% is added, while 3.0% of sulfur is used also, which itself improves aging resistance. Under these conditions, the benefits obtained from vulcanization control may well exceed the oxidizing effect, and it was on this ground that the following experiments were made.

2. DIPHENYLGUANIDINE STOCKS

Experiments were made with stocks accelerated with diphenylguanidine, well known as an accelerator giving poor aging resistance, to demonstrate the adequacy of the effect sought. The base stocks used comprised pale crepe 100, sulfur 3, zinc oxide 5 to 10, diphenylguanidine 1, and various analogous mixtures. To these were added proper quantities of vulcanization controllers such as described above, including ammonium persulfate, benzoyl peroxide, nitrobenzene, picric acid,

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artificial musk (xylene type), *m*-dinitrobenzene and *sym*-trinitrobenzene. Oxygen bomb aging tests were made.

Ammonium Persulfate and Benzoyl Peroxides.—As little as 0.01% of these reagents is sufficient to have a controlling effect on vulcanization, but as both are powerful oxidizing agents, the smallest amounts lead to vigorous attack on the rubber, and the application of such controllers does not seems to be feasible.

Artificial Musk.—This compound is more or less unstable, and its action in controlling vulcanization ranks second to that of the two agents above. Protection against aging is therefore not satisfactory.

sym-*Trinitrobenzene.*—Vulcanization control is obtained with proportions only up to 0.5% of this compound, and if the amount is increased beyond this, oxidizing effects might be anticipated. Practical application is thus more or less unsatisfactory.

Nitrobenzene.—Little danger of oxidizing effects is to be anticipated with this compound but on the other hand it is deficient in its effect in controlling vulcanization.

Picric Acid.—Differing from the previous substances, picric acid retards vulcanization considerably because of its acidic nature. The risk of incomplete vulcanization is thus too great to make it feasible to use this reagent.

m-*Dinitrobenzene.*—This compound is of medium effect, giving sufficient control of vulcanization for practical use, while in the proportion of 1.0% of the rubber any oxidizing effect is scarcely to be feared. In the following experiments, this substance is compared with the well known antioxidant, aldol-α-naphthylamine, and the effects of combining the two substances have also been studied.

Using purified *m*-dinitrobenzene (m.p., 82.5° C.), recrystallized by adding cold water to an ethyl alcohol solution of the crude product, mixings were prepared as in Table I.

TABLE I

Base stock: pale crepe 100, sulfur 3, whiting 100, zinc oxide 10, diphenylguanidine 1, to which were added:

	No. 1	No. 2	No. 3	No. 4
Aldol-α-naphthylamine	—	1	—	0.5
m-Dinitrobenzene	—	—	1	0.5

These compounds were vulcanized in a press at 147° C. (50 lb. per sq. in. steam), and gave the following test results:

TABLE II

Vulc., minutes	Tensile strength (kg. per sq. in.) No. 1	No. 2	No. 3	No. 4	Elongation at break (%) No. 1	No. 2	No. 3	No. 4
10	166	164	164	185	534	556	562	594
20	174	169	173	173	521	536	550	552
30	166	162	151	168	506	524	508	536
40	160	154	156	165	503	520	521	526
50	143	133	142	—	491	495	501	—

Vulc., minutes	Hardness (Shore) No. 1	No. 2	No. 3	No. 4	Load at 300% elongation (kg. per sq. cm.) No. 1	No. 2	No. 3	No. 4
10	56	56	55	53	58	53	50	52
20	60	60	60	57	66	52	60	60
30	61	61	61	60	68	64	64	63
40	62	62	62	60	68	63	65	67
50	63	62	62	—	66	61	63	—

After aging in the oxygen bomb at 300 lb. per sq. in. pressure, 60° C., for 3 days, the strengths of these samples were determined. The following results for three samples near optimum vulcanization have been obtained:

TABLE III

Vulc., minutes	Tensile strength				Elongation at break				Load at 300%			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
10	136	151	150	167	543	546	566	561	51	55	47	83
20	132	148	151	162	500	500	519	522	59	65	58	97
30	118	144	148	156	498	486	515	498	59	70	63	105

Consideration of the above results suggests that the age-resisting action of *m*-dinitrobenzene is superior to that of aldol-α-naphthylamine, and it is an interesting point that the combination of the two preservatives is far more effective than either used separately.

It is to be noted, further, that the *m*-dinitrobenzene rubbers have a low modulus, and so feel soft and flexible, therefore surface cracking is scarcely appreciable in light-exposure tests.

The following compounds, indicated in Table IV, were analyzed as indicated by the results in Table V. The iodine values were determined by the method of Kemp, Bishop and Lackner[2].

TABLE IV

Base stock: pale crepe 100, sulfur 3, zinc oxide 10, diphenylguanidine 1, with:

	No. 1	No. 2
m-Dinitrobenzene	—	1

TABLE V

Mixings above vulcanized at 147° C. for 40 minutes

	No. 1	No. 2
Acetone extract (%)	3.90	4.01
Chloroform extract (%)	0.57	0.43
Free sulfur (%)	0.44	0.57
Combined sulfur (%)	2.07	1.94
Ash (%)	9.22	9.15
Iodine value	330.8	315.6

In view of the above data, it would be incorrect to consider that vulcanization has been retarded by the addition of *m*-dinitrobenzene, the more reasonable hypothesis being that some vulcanization by *m*-dinitrobenzene has replaced part of the vulcanization by sulfur. As a result, vulcanization has been controlled, or stopped in the primary stage, and not advanced to the secondary stage.

Accelerated aging due to copper can be inhibited by means of some antioxidants on the market. According to our experiments, it has been found that *m*-dinitrobenzene in diphenylguanidine stocks is not sufficient to retard aging due to copper.

On the other hand, it is known that antioxidants, in general reducing agents, act as retarders of oxidation and drying of oil varnishes applied to rubber goods containing them; *m*-dinitrobenzene does not have this effect, so that the period of drying of oil varnishes on such rubbers is much shortened.

3. *m*-DINITROBENZENE WITH OTHER ACCELERATORS

Experiments have been made similar to the foregoing with mercaptobenzothiazole, tetramethylthiuram disulfide, piperidinium pentamethylenedithiocarbamate and Vulkacit 576. It has been found that no special improvement in age resistance occurs in these cases comparable with that in the presence of diphenylguanidine. In the case of mercaptobenzothiazole, on the contrary, there is a tendency to reduce the resistance to aging.

Using purified *m*-dinitrobenzene as before (m.p., 66 to 83.5° C.), the following results have been obtained:

TABLE VI

Base stock: pale crepe 100, sulfur 3, zinc oxide 10, stearic acid 1, mercaptobenzothiazole 0.8, with:

	No. 1	No. 2
m-Dinitrobenzene	—	1

Vulcanization at 141° C. (40 lbs. per sq. in.)

TABLE VII

TEST RESULTS ON THE NEW RUBBERS

Vulc., minutes	Tensile strength (kg. per sq. cm.)		Elongation at break (%)		Hardness (Shore)		Load at 600% (kg. per sq. cm.)	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
10	58	62	860	895	29	30	11	14
20	115	124	870	824	33	34	34	35
30	128	123	796	787	36	36	40	40
40	121	130	782	786	36	37	43	43
50	126	125	786	775	37	37	43	44

After aging in the oxygen bomb at 300 lbs. per sq. in., 60° C., for 6 and 12 days, respectively, the following results were obtained:

TABLE VIII

Aging days	Vulc., minutes	Tensile strength		Elongation		Load at 600%	
		No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
6	30	164	181	734	753	72	75
6	40	150	187	698	744	85	86
6	50	143	164	694	705	83	90
12	30	168	94	668	552	—	—
12	40	161	103	672	588	—	—
12	50	142	77	666	566	—	—

4. STABILITY OF *m*-DINITROBENZENE

Though *m*-dinitrobenzene in itself is stable and is not decomposed by heating, its stability may be considerably altered in either direction according to the impurities present, in a manner similar to that of stabilizing explosives by adding various substances to them. It may, therefore, be argued that the remarkable phenomenon of increased age resistance is a selective action, specific to diphenylguanidine, which behaves as a stabilizer of *m*-dinitrobenzene. Similarly the other accelerators may be regarded as decomposers. To throw light on this suggestion, tests have been made on the stability of *m*-dinitrobenzene, alone and when mixed with various rubber chemicals and with stabilizers used in explosives.

The Abel test at 150° C. for stability of explosives was employed, and as *m*-dinitrobenzene is not easily decomposed at this temperature, a mixture of

m-dinitrobenzene 0.2 and zinc oxide 1.0 was used. The iodo-starch paper changed color in 18 to 20 minutes with the above mixture. Substances increasing this period were regarded as stabilizers, and substances shortening it as decomposers.

It has been found that diphenylguanidine acts as an appreciable stabilizing agent, while all other accelerators examined have more or less decomposing effect.

Other stabilizing agents discovered by the test include, in particular, diphenylamine, which is known to be effective in stabilizing explosives and various amines, metallic soaps and mineral oils.

Experiments have therefore been made with *m*-dinitrobenzene stabilized with diphenylamine to ascertain if the decomposing effect of mercaptobenzothiazole persisted in such conditions. It has been found that age resistance superior to that given by aldol-α-naphthylamine can be obtained.

Using purified *m*-dinitrobenzene as before (m.p., 75.3° to 85.5° C.), and purified diphenylamine (m.p., 51.7° to 52.5° C.), recrystallized from hot water, the following mixings have been prepared:

TABLE IX

Base stock: pale crepe 100, sulfur 3, zinc oxide 10, stearic acid 1, mercaptobenzothiazole 0.8, with:

	No. 1	No. 2	No. 3
m-Dinitrobenzene	1	1	—
Diphenylamine	—	0.1	—
Aldol-α-naphthylamine	—	—	1

Vulcanization, at 141° C. (40 lbs. per sq. in.)

TABLE X

Vulc., minutes	Tensile strength (kg. per sq. cm.) No. 1	No. 2	No. 3	Elongation at break (%) No. 1	No. 2	No. 3
10	104	123	130	888	904	871
20	155	164	139	814	803	824
30	137	158	147	764	774	778
40	149	143	148	772	750	769
50	149	143	149	771	765	778

Vulc., minutes	Hardness (Shore) No. 1	No. 2	No. 3	Load at 600% (kg. per sq. cm.) No. 1	No. 2	No. 3
10	35	35	36	20	20	25
20	40	40	40	40	45	45
30	40	41	40	48	53	52
40	40	41	40	51	55	53
50	40	41	40	49	52	51

After aging in the oxygen bomb at 300 lbs. per sq. in., 60° C., for 6 days and 12 days, respectively, the following results were obtained:

TABLE XI

Aging days	Vulc., mins.	Tensile strength No. 1	No. 2	No. 3	Elongation No. 1	No. 2	No. 3	Load at 600% No. 1	No. 2	No. 3
6	20	173	186	187	673	675	663	111	120	128
6	30	151	167	183	667	665	668	105	117	122
6	40	126	134	176	655	639	676	92	100	108
12	20	188	180	176	684	664	654	118	125	129
12	30	144	175	160	649	656	642	110	128	129
12	40	120	132	140	651	629	634	90	113	113

Thus if a small proportion of a suitable stabilizer is added, whatever accelerator may be used, a reduction of aging in the presence of *m*-dinitrobenzene can be shown, the results for this substance comparing favorably with those for aldol-α-naphthylamine. Further, as rubbers of lower modulus are obtained, protection against surface cracking may be expected. It seems probable that if these vulcanization-controlling agents were in regular technical use, their manufacture would be simplified and their cost would compare favorably with that of well known antioxidants.

5. SUMMARY

(1) Considering that low-sulfur vulcanization gives high resistance to aging, because vulcanization does not go beyond the primary stage, it has been sought to effect this control in stocks accelerated with diphenylguanidine. *m*-Dinitrobenzene has been selected from a number of possible agents as a reliable controller; other agents which retard vulcanization and have weak control effect or active oxidizing effect were rejected.

(2) From a comparison of *m*-dinitrobenzene and aldol-α-naphthylamine in diphenylguanidine stocks, successful aging resistance has been observed. Mechanical tests were carried out before and after bomb aging, and chemical analyses were made of the vulcanized rubbers to throw light on the vulcanization mechanism and the reasons for improved resistance to aging.

(3) Parallel experiments with other accelerators failed to reveal improved aging resistance, and in the presence of mercaptobenzothiazole in particular, *m*-dinitrobenzene acts as an oxidizing agent.

(4) Tests of the stability of *m*-dinitrobenzene, alone and when mixed with various reagents, by the Abel test for stability of explosives have shown that the stability depends on the purity of the compound. Diphenylguanidine is effective as a stabilizer of *m*-dinitrobenzene, while other accelerators act as decomposers, thus providing a reason for the age resistance observed with diphenylguanidine.

As a result of the stability tests, it has been found that various amines, soaps and mineral oils are effective as stabilizers of *m*-dinitrobenzene. As an instance of their application, aging tests have been carried out on rubber compounds accelerated with mercaptobenzothiazole and containing *m*-dinitrobenzene stabilized with diphenylamine. It has been found that the age resistance is much improved and is comparable with that obtained in the presence of aldol-α-naphthylamine.

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RUBBER–VULCANIZING PROPERTIES OF COLLOIDAL CARBONS *

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I. COURSE OF VULCANIZATION

Introduction

Previous Work.

The literature abounds in references to the retarding effect of carbon black on vulcanization.

Twiss and Murphy[1], for a rubber 100, sulfur 10 mixing, gave figures showing a retardation of from about 105 to 155 minutes. They ascribed this to removal by adsorption of part of the natural accelerator of the rubber. The same authors also pointed out the accelerating influence in the same mixture of Thermatomic carbon, a result which they describe as hardly to be expected from the nature of the material. Twiss and Murphy used ten volumes of pigment in each case, and their criterion of vulcanization was maximum tensile strength.

Goodwin and Park[2] carried out studies of various carbons, not only in rubber-sulfur, but also in litharge, mercaptobenzothiozole, diphenylguanidine, hexamethylenetetramine and ethylideneaniline accelerated mixings. They state: "A highly absorptive carbon removes the curing agent from the rubber to such an extent that it is, for practical purposes, impossible to get a satisfactory rubber gel on vulcanization." The criterion of vulcanization used by Goodwin and Park was time to maximum tensile product. Hand tests were employed also.

Shepard[3] states: "The writer knows of no case where channel black does not retard cure."

Cadwell and Temple[4] state: "Carbon black . . . retards vulcanization so greatly that its use would have been impracticable without accelerators of some kind."

Carson and Sebrell[5] state: "The addition of black to a rubber-sulfur mix slows down the time of cure, but the addition of black to a rubber-sulfur-zinc oxide mix accelerates, evidently owing to the liberation of an accelerator."

These references are not offered as comprehensive, but rather illustrative. The purpose of the present study is to examine in a preliminary way the relationships between vulcanizing behavior and other properties of typical carbons, and secondly, to examine some of the factors by which these vulcanizing properties may be controlled or altered.

Criteria of State of Vulcanization.

The coefficient of vulcanization is deemed too little representative of physical strength. Maximum tensile strength has been thought, in most cases, to represent a state of vulcanization too far advanced for good aging. Hand testing, although still widely employed and of undoubted utility, is not quantitatively expressible. Earlier studies[6] and subsequent experience have indicated that time to maximum

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 33, pages 484-504.

tensile product, which occurs at an earlier point than maximum tensile strength in nearly every case, is in general not far removed from best technical vulcanization[7], and has therefore been selected as the general basis for rate of vulcanization comparisons.

TABLE I

PROPERTIES OF CARBON USED IN THIS STUDY

Carbon	pH‡	X*	V†	Type of carbon
A	11.2	4.5	0.2	Super Deactivated Colloidal Carbon (HS-332)
B	9.3	2.5	0.7	Furnace Carbon (Fumonex)
C	9.1	2.6	0.7	Furnace Carbon (Gastex)
D	8.2	4.1	0.6	Acetylene Carbon (Shawinigan)
E	8.2	1.1	0.6	Thermal Carbon (P-33)
F	6.9	3.9	0.8	Acetylene Carbon (German)
G	6.0	6.0	3.4	Deactivated Colloidal Carbon (1AAA)
H	5.7	5.3	3.4	German Carbon (CK-3)
I	5.5	8.0	3.7	Mildly Deactivated Colloidal Carbon (1AA)
J	5.2	44.1	7.2	High Color Colloidal Carbon (Super Spectra)
K	5.0	51.8	6.0	Medium Color Colloidal Carbon (Superba)
L	4.8	8.6	4.2	"Quick Curing" Colloidal Carbon (Ultramicronex)
M	4.6	17.3	4.2	Special Colloidal Carbon (95-R)
N	4.5	10.1	5.0	Standard Colloidal Carbon (Micronex)
O	4.4	10.0	5.1	Easy Mixing Colloidal Carbon (Micronex W-6)
P	3.8	16.8	5.6	"Slow Curing" Colloidal Carbon (Micronex Mark II)
Q	3.1	96.0	12.8	Highest Color Colloidal Carbon (Royal Spectra)
R	2.6	58.4	12.0	Long Ink Colloidal Carbon (Peerless)

* X = Adsorption Index[10]. † V = Volatile matter[11]. ‡ pH = Sludge pH[15].

TABLE II

VARIOUS CARBONS IN RUBBER-SULFUR

Smoked sheet	100
Sulfur	10

1931 Tests (vulcanizing temperature 288° F.)

	Time to maximum tensile product	Time to maximum tensile strength	Hand	Mean Optimum cure
No carbon	5 hrs.	5 + hrs.	3 hrs.	4.3 hrs.
I (36%)	2½ "	2½ "	2 "	2.3 "
N (36%)	3 "	3 "	2½ "	2.8 "
Q (36%)	3½ "	4½ "	2 "	3.3 "

1938 Tests (vulcanizing temperature 316° F.)

No carbon	50 min.	60 min.	45 min.	52 min.
L (40%)	30 "	35 "	30 "	32 "
J (30%)	45 "	50 "	50 "	48 "
Q (30%)	25 "	40 "	40 "	35 "

It scarcely needs mention that any property passing through a maximum value against time of vulcanization is inherently an unsatisfactory vulcanization criterion because at exactly the point where the state of vulcanization should most nicely be determined, the rate of change becomes zero. It is to be hoped that the Gibbons, Gerke and Tingey T-50 test[8] will receive wider study so that, if possible, correction factors can be applied which will make it universally valid[9]. It is of course free from the objection just mentioned.

In Table I are shown the carbons used in this study. The general description is supplemented by the trade names in order to facilitate positive identification.

Rubber-Sulfur Mixings.

The results obtained in these laboratories are at variance with the literature. Colloidal carbons were found, without exception, to accelerate and not retard vulcanization.

The results of three separate series are shown in Table II and III. Tensile strength and tensile product relationships are shown in Figure 1, in which P.G.

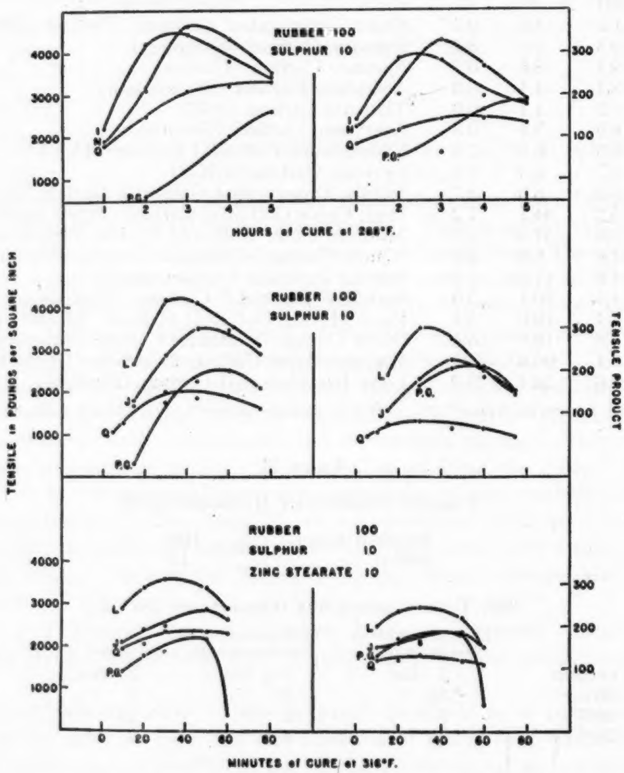

FIG. 1.

signifies the unpigmented compound. These Tables and Figure permit the following conclusions:

(1) In all cases colloidal carbon showed acceleration of vulcanization compared to the pure gum base.

(2) There was no correlation between pH or other chemical properties and degree of acceleration. The completely dissimilar colloidal carbons, L and Q, showed similar times of vulcanization.

(3) The addition of 10% of zinc stearate shortened the vulcanization in all cases, but more so in the case of the pure gum than in the case of the colloidal carbon-reinforced mixing. Thus, the effect of zinc stearate was to iron out as well as to accelerate vulcanization.

(4) A study of Figure 1 reveals that the colloidal carbons gave greatly improved physical properties with the single exception of carbon Q.

Behavior of Various Carbons in Diphenylguanidine Test Compound.

For upwards of fifteen years it has been found that a diphenylguanidine (D.P.G.) accelerated test compound, containing no fat acid and somewhat low in D.P.G., served best to distinguish between rate of vulcanization of various carbons. In Table IV are shown the vulcanizing properties in this mixing for a range of carbons which have been used in rubber compounding and which exhibit *p*H values

TABLE III

VARIOUS CARBONS IN RUBBER + SULFUR + ZINC STEARATE

Smoked sheet	100
Sulfur	10
Zinc stearate	10

Vulcanizing temperature 316° F.

Carbon	Time to maximum tensile product	Time to maximum tensile strength	Hand	Mean Optimum cure
No carbon	35 min.	40 min.	30 min.	35 min.
L	27 "	30 "	25 "	27 "
J	35 "	40 "	30 "	35 "
Q	20 "	40 "	25 "	28 "

TABLE IV

*p*H OF CARBONS VERSUS RATE OF VULCANIZATION

D.P.G. Test Mixing

Smoked sheet	100
Carbon	38
Zinc oxide	3.2
Sulfur	5.4
D.P.G.	0.8

Carbon	*p*H	Optimum time (min.)	Modulus	Tensile strength	Elongation	Tensile product	Shore hardness
None	—	27	250	3425	770	265	47.5
P	3.8	60	900	3925	675	265	59.0
N	4.5	35	1000	4375	700	306	57.5
L	4.8	28	1000	4600	720	331	59.0
F	6.9	27	750	4000	710	284	59.5
E	8.2	14	375	4125	780	322	50.0
D	8.2	23	1550	3700	585	216	64.0
B	9.3	25	925	3800	635	242	56.0
A	11.2	20	800	4200	710	298	62.5

ranging from 3.8 to 11.2. Both colloidal carbons and thermal decomposition carbons are included, as well as socalled furnace type carbons. Details of adsorption and volatile indices are shown in Table I.

It will be seen that some of the carbons retarded the D.P.G. vulcanization, whereas others accelerated. The question arises as to whether these differences can be related to other properties.

Correlation of Rate of Vulcanization with pH *Properties.*

When the values for time of optimum vulcanization shown in Table IV were plotted against volatile matter or against adsorption index, or against combinations of these two indices, it was found that fairly good correlation obtained for

those carbons which retarded, but that there was a complete absence of correlation for those carbons which showed no interference with the diphenylguanidine. On the other hand, when time of vulcanization was plotted against hot sludge pH values of the carbons, a correlation was obtained as shown in Figure 2. The single exception was found to be thermal decomposition carbon E, which accelerated to a degree even greater than would be expected from its pH value. No detailed investigation on this point has been made. On acetone extracting carbon E, it was found that the pH declined, thus affording a slight indication that possibly the tarry matter present in this carbon might have exerted an accelerating effect.

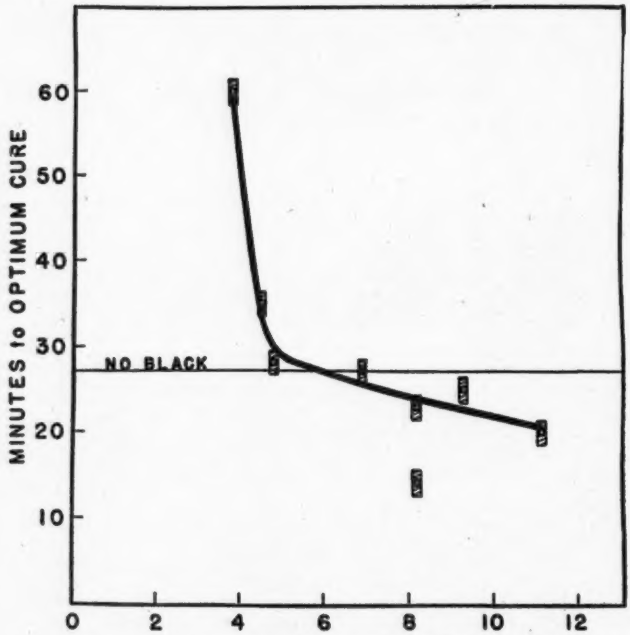

FIG. 2.—pH of carbon *vs.* optimum cure. D.P.G. compound.

II. CONTROL

Effect of Accelerator.

The vulcanizing characteristics of various colloidal carbons may be controlled either by choice of accelerator or by zinc and fat acid adjustment, or by artificial change in the surface chemistry of the carbons themselves. The effect of accelerator will be first discussed.

In Table V the various compounds are summarized. In Table VI will be found the experimental data from which the following conclusions have been drawn.

(1) Colloidal carbons N and I, representing respectively standard rubber carbon and a less adsorptive carbon, were brought by litharge compound No. 1 to the same rate of vulcanization, and in the case of mercaptobenzothiazole compounds No. 2 and 4, the differences were largely, although not entirely, ironed out.

TABLE V

EFFECT OF ACCELERATOR ON VULCANIZATION VARIATIONS IN CARBONS

LIST OF COMPOUNDS

	1	2	3	4	5	6	7	8	9	10	11
Rubber	100	100.0	100.00	100	100.0	100.00	100.0	100	100	100.0	100.00
Carbon	40	50.0	50.00	50	38.0	44.00	50.0	45	45	36.0	40.00
Zinc oxide ...	—	5.0	—	8	3.2	9.00	5.0	—	5	5.0	5.00
Litharge	30	—	8.35	—	—	—	—	13	6	—	—
D.P.G.	—	—	—	—	0.8	—	—	—	—	—	—
Mercaptobenzothiazole .	—	1.2	—	1	—	—	1.0	—	—	1.0	—
808	—	—	—	—	—	1.00	—	—	—	—	—
Stearic acid .	—	4.0	4.00	4	—	—	3.5	—	10	—	—
Zinc laurate .	—	—	—	—	—	1.00	—	—	—	—	—
Pine tar	4	3.0	2.00	3	—	3.25	3.8	—	—	—	3.00
Sulfur	5	2.8	3.50	3	5.4	3.25	3.5	3	4	3.0	4.00
Antioxidant .	—	—	—	1	—	1.10	1.3	—	—	—	—
Tuads	—	—	—	—	—	—	—	—	—	—	0.25

NOTE *re* PHYSICAL PROPERTIES

Modulus = tension at 300% elongation in pounds per sq. inch. (To convert to kg. per sq. cm., multiply by 0.0703.)
Tensile strength = tension at break in pounds per sq. inch.
Tensile product = product of tensile and elongation at break, divided by 10,000.
Test-pieces used were dumb-bell, ¼ inch width, 1 inch bench marks, gauge 0.100 inch.
Testing machine was Scott, at 20 inches per minute.
Temperature and ***humidity*** were 82° F., and 45%.
Reduction of stress-strain observations: Best three elongations out of five method[12].
Criteria of hand tests:

(1) Liveliness on rapid jiggling in Region C of the curve.
(2) Hand tear testing.
(3) Scissors crunch.
(4) Set.
(5) Twanging when stretched to Region C.

TABLE VI

TIME TO OPTIMUM VULCANIZATION

Accelerator	Compound No.	Carbon	Time of optimum vulcanization
Carbons N and I with Litharge and Mercaptobenzothiazole			
Litharge	1	N	40 min. at 274° F.
"	1	I	40 " " 274° F.
Mercaptobenzothiazole	2	N	30 " " 274° F.
"	2	I	30 " " 274° F.
"	4	N	35 " " 274° F.
"	4	I	30 " " 274° F.
Carbons C, E, H, L, with Litharge			
Litharge	3	C	12.5 " " 288° F.
"	3	E	12 " " 288° F.
"	3	H	12 " " 288° F.
"	3	L	13 " " 288° F.
Carbons O and P with D.P.G., 808, and Mercaptobenzothiazole			
D.P.G.	5	O	25 " " 288° F.
"	5	P	40 " " 288° F.
808	6	O	30 " " 288° F.
"	6	P	40 " " 288° F.
Mercaptobenzothiazole	7	O	30 " " 288° F.
"	7	P	35 " " 288° F.
Carbons N and H with D.P.G. and Mercaptobenzothiazole			
D.P.G.	5	N	35 " " 288° F.
"	5	H	20 " " 288° F.
Mercaptobenzothiazole	2	N	35 " " 274° F.
"	2	H	25 " " 274° F.

(2) Carbons C, E, H, and L, representing a wide range, both as regards method of preparation and pH properties, were reduced by litharge in compound No. 3 to practically identical vulcanizing rates.

(3) Carbons O and P, representing two distinct types of colloidal carbon differing in rate of vulcanization as well as in particle size and milling behavior, showed, when tested in D.P.G. 808 (butyraldehydeaniline), and mercaptobenzothiazole treads, differences in rate of vulcanization which were greatest for the D.P.G., intermediate for 808, and least for mercaptobenzothiozole.

(4) Carbons N and H, tested in D.P.G. and mercaptobenzothiozole compounds No. 5 and 2, respectively, again showed superior ironing out for mercaptobenzothiazole.

In sum, under favorable conditions (proper zinc and fat acid proportions), mercaptobenzothiozole compounds are definitely superior to the guanidine compounds in ironing out rate of vulcanization differences of various carbons. There still remain, with carbons of differing pH properties, considerable residual vulcanizing differences in mercaptobenzothiozole treads. These differences are markedly greater than in the case of properly compounded litharge formulas.

TABLE VII

Carbon	pH	Stearic acid	Optimum vulcanization at 288° F.	Modulus	Tensile strength	Remarks
N	4.5	0	35 min.	900	4250	Best
		0.4	35 "	875	4200	
		4.0	35 "	725	4125	
P	3.6	0	60 + "	1000	4000	
		0.4	60 "	975	4000	
		4.0	55 "	950	4300	Best

Notes:

(1) With carbon N of moderate pH and relatively low adsorption, the addition of 4% of fat acid did not improve vulcanizing rate or properties, but tended to lower them. (There was, of course, present approximately 1.5% of natural fat acid in the smoked sheet.)

(2) The slow vulcanizing carbon of low pH was, on the contrary, improved by the addition of 4% of fat acid, both as regards quality and rate of vulcanization, the former being, however, the more significant result of the addition of the stearic acid.

Effect of Zinc Oxide and Fat Acid Content.

In this section the effect on the vulcanizing properties of colloidal carbons of zinc oxide and of fat acid, with various types of accelerators, will be illustrated.

Rubber-Sulfur.—In Table III the effect of the addition of 10% on the rubber of zinc stearate was seen to consist of an accelerating action which was pronounced in the case of the rubber-sulfur control mixing containing no carbon, but comparatively slight in the presence of various colloidal carbons.

D.P.G.—Test mixing No. 5 was used in conjunction with carbons N and P, respectively, standard and slow vulcanizing grades. Stearic acid was added with results as shown in Table VII.

Litharge.—Compounds No. 8 and 9 were used with carbons L, N, J, and Q, ranging from very quick vulcanizing rubber carbon to the highest intensity color carbon of very low pH and normally considered to be incapable of proper vulcanization in rubber. The results, with increasing addition of stearic acid, are summarized in Table VIII.

Fat Acid Requirements with Mercaptobenzothiazole Tread Compound Using Various Carbons.—The carbons here studied, G, I, N and P, although all of similar particle size, differ widely in pH properties. Formula No. 10 was used as base and stearic acid in various amounts added up to 6%. The resulting vulcanization and tensile properties are shown in Table IX.

TABLE VIII

Carbon	Fatty acid	Optimum vulcanization at 288° F.	Modulus	Tensile strength	Tensile product	Remarks
L......	0	15 min.	1275	4250	250	
	6	20 "	1100	4550	300	Best result.
	10	20 "	1000	4400	305	M. and T. off.
N......	0	10 "	1150	4100	240	
	6	20 "	925	4400	295	Best result.
	10	20 "	825	4350	310	M. and T. off.
J	0	10 "	1250	3450	285	
	6	20 "	925	4750	315	Best result.
	10	20 "	750	4700	345	M. and T. off.
Q......	0	10 "	1800	3000	120	
	6	10 "	1550	4200	225	
	10	15 "	1400	4700	290	Best result.

Notes:

(1) In the absence of added stearic acid all of the carbons gave inferior properties; the greater the specific surface, and in general, the lower the *p*H the greater the drop in quality.

(2) Carbons L, N, and J developed full properties with 6% of added acid, but carbon Q required 10 parts and might have done still better with more.

(3) The apparent retardation of vulcanization with increasing stearic acid should be interpreted as a measure of vulcanization development rather than one of retardation. Without fat acid the properties decay practically from the earliest vulcanization. This distinction is believed to be important.

(4) In the presence of sufficient fat acid the highest color carbon developed physical properties fully the equal of standard rubber carbon, and indeed with higher modulus.

TABLE IX

Carbon	*p*H	Stearic acid	Optimum vulcanization at 288° F.	Tensile strength	Remarks
G..........	6.0	0	15 min.	3000	
		2	20 "	4500	
		4	15 "	4700	Best.
		6	10 "	4600	
I	5.5	0	15 "	2400	Bad vulcanization.
		2	35 "	4200	
		4	20 "	4700	Best quality.
		6	15 "	4700	Blooms. Fastest.
N..........	4.5	0	25 "	2200	Bad vulcanization.
		2	35 "	4000	
		4	25 "	4750	Best.
		6	20 "	4700	Blooms badly. Fastest.
P..........	3.8	0	20 "	2000	
		2	35 "	3700	
		4	35 "	4650	
		6	25 "	4800	Best in this region.

Notes:

(1) In the absence of any added fat acid, all carbons showed poor properties, the lower the *p*H the worse.

(2) The addition of 2% acid has vastly improved the properties. The apparently longer time to optimum vulcanization is more accurately to be interpreted as vulcanization development rather than vulcanization retardation (See Table VIII).

(3) With the addition of 4% of stearic acid, the properties of the first three carbons have reached full development.

(4) The addition of 6% acid has gone beyond the optimum point for the first three carbons, but has brought the fourth, a low *p*H carbon, to its best properties. Time of vulcanization with 6% added acid is shorter than with 4% acid, showing genuine acceleration.

(5) In addition to the conclusion that different types of carbon require different fat acid additions, it should be emphasized that shortage of fat acid is to be recognized less by disturbance in time of vulcanization than by injury to the quality.

(6) The effect of adequate fat acid additions in ironing out differences in carbons is shown in Figure 3 in which the tensile strength and tensile product curves for the four carbons are brought together.

(7) The effect of increasing fat acid additions on apparent rate of vulcanization is shown in Figure 4 for carbon P of the above series. This figure shows clearly the distinction between apparent retardation of vulcanization and vulcanization development as defined above.

Varying Zinc Oxide Content in Mercaptobenzothiazole Tread Containing 4% Added Stearic Acid.—The base compound for the following series was No. 2, without zinc or fat acid. The carbon used, P, was a low *p*H type (3.8). Results are shown in Table X.

Will Addition of Fat Acid Compensate for Low Zinc?—The base compound was the same as above (No. 2). The same carbon was used also. The results obtained with 0.25% of added zinc oxide, without acid, compared with the same to which 4% stearic acid was added, are shown in Table XI.

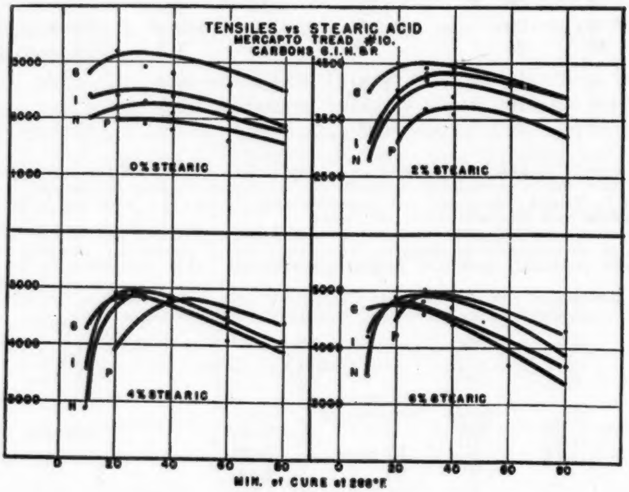

Fig. 3.

TABLE X

Zinc oxide		Stearic acid		Optimum vulcanization	Modulus	Tensile strength	Tensile product	Shore hardness
Total	As soap	Total	As soap					
0.25	0	4	0	20 min.	525	2650	196	53
0.50	0.50	4	4	15 "	625	3700	286	55
0.75	0.50	4	4	20 "	800	4150	317	58
5.00	0.50	4	4	22 "	975	4350	321	61

Notes:

(1) All mixings excepting that with 5% zinc oxide showed reversion on the longer times. Three-quarters of 1% of total zinc oxide was clearly not enough in the presence of 50% carbon.

(2) The time of optimum vulcanization was not sensibly altered through wide variations in zinc oxide.

(3) Physical properties were, however, profoundly influenced. Tensile strength, modulus, tensile product and hardness all rose with increasing zinc content.

(4) This series indicates that with normal fat acid content, shortage of zinc is reflected in poor (physical) vulcanization rather than in slow vulcanization.

A similar comparison with 0.75% of zinc oxide is summarized in Table XII.

Comparative Zinc Oxide Requirements of High and Low pH *Carbons in Mercaptobenzothiazole Tread.*—In Figure 5 is shown the effect on tensile properties at optimum vulcanization of varying zinc oxide dosages with a rubber carbon of *p*H 4.8 compared to a type with a *p*H of 3.8. In all cases 4.5% by weight on the crude rubber of the zinc stearate was added, corresponding to a constant stearic acid addition of approximately 4% on the rubber. Additional amounts of free zinc oxide were added, but only total percentages of zinc oxide are shown in the figure. The base compound used was No. 2 without zinc oxide or fat acid.

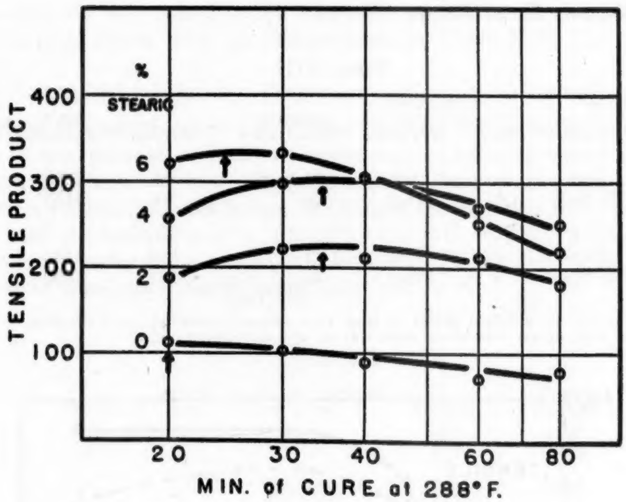

FIG. 4.—Stearic acid *vs.* cure. Mercapto tread. Carbon P.

TABLE XI

Zinc oxide		Stearic acid					
Total	How added	Total	How added	Optimum vulcanization	Modulus	Tensile strength	Shore hardness
0.25	Free	0	—	30 min.	700	2700	56
0.25	"	4	Free	20 "	525	2650	53

Notes:

(1) The low zinc oxide was reflected in poor vulcanization, involving tensile properties far below those inherent in this type of tread mixing.

(2) The addition of 4% stearic acid shortened the time of vulcanization but did not improve the physical properties which were in fact lower in modulus, tensile strength and hardness. This is an example where vulcanization has been made quicker but poorer.

(3) In the absence of sufficient zinc oxide the addition of stearic acid did not improve physical properties.

TABLE XII

Zinc oxide		Stearic acid					
Total	How added	Total	How added	Optimum vulcanization	Modulus	Tensile strength	Tensile product
0.75	0.5 Soap	4	Soap	20 min.	800	4150	317
0.75	Soap	6	"	22 "	850	4125	309

Notes:

(1) In the first compound (the control) 4% of stearic acid was added as zinc stearate, thus providing 0.5 as zinc oxide in solution. To this was added 0.25% zinc oxide in free powdered condition in order to neutralize the natural fat acid in the rubber. Thus, there was present sufficient total fat acid to react with all of the zinc oxide present. The total amount of zinc oxide employed was designed to be on the low side, which is evidenced by the low tensile properties.

(2) In the second compound, while keeping the total zinc oxide constant, the fat acid was raised (soap form) to 6% on the rubber instead of 4%. The object of this change was again to determine whether a slight insufficiency of zinc oxide could be compensated in the presence of carbon, by an increase in fat acid.

(3) Again there was no improvement either in time or quality of vulcanization.

Comparative Effect of Adding Fat Acid in Soap Form and as such in Mercaptobenzothiazole Tread Mixing (No. 2).

TABLE XIII

Zinc oxide Total	Zinc oxide How added	Stearic acid Total	Stearic acid How added	Optimum vulcanization	Modulus	Tensile strength	Tensile product
(*a*) Low zinc							
0.75	Free	4	Free	20 min.	800	3900	292
0.75	0.5 Soap	4	Soap	20 "	800	4150	317
(*b*) High zinc							
5	Free	4	Free	22 "	900	4350	316
5	0.5 Soap	4	Soap	22 "	975	4350	321

Notes:
(1) With zinc low, its addition partly in soap form seemed somewhat more effective.
(2) However, with excess zinc oxide there was no appreciable difference.

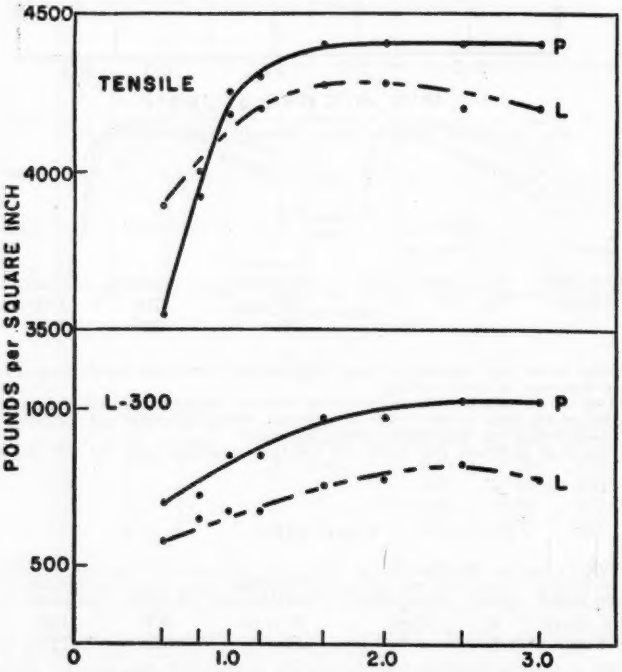

FIG. 5.—Zinc oxide *vs.* cure. Mercapto tread.

Notes:
(1) The outstanding conclusion from this series is that for both carbons vulcanization was impossible for values of total zinc less than 1% on the rubber. Between 1% and approximately 2% the vulcanizations slowly improved.
(2) The low *p*H carbon was more sensitive to zinc shortage than was the high *pH* carbon. For zinc additions beyond 2% the 4.8 *p*H carbon gave indications of some falling off[13] in tensile properties to an extent greater than in the case of the 3.8 *p*H carbon.
(3) An inspection of both ends of the tensile-zinc oxide curve suggests that the low *p*H carbon required a larger addition of total zinc in order to provide for its greater adsorptive requirements.
(4) The higher ultimate tensile strength for the low *p*H carbon, when zinc was present in ample amount, is not to be ascribed solely to its chemical or adsorptive properties, since there is evidence that its particle is somewhat smaller than that of the higher *p*H carbon.

Fat Acid Requirement of High and Low pH *Carbons in Tuads Tread Compounds.*—N (*p*H 4.5) and P (*p*H 3.8) were compared in compound No. 11 accelerated with Tuads, with the results shown in Table XIV.

Artificial Control of Vulcanizing Properties of Carbon by Deactive Heating.

The effect of such treatment of rubber carbons has already been communicated[14]. It was thought of interest, however, to add data showing the extent to which a high color carbon, which ordinarily displays very poor vulcanizing properties in rubber compounds, can be changed through deactive heating from a strongly acid *p*H condition to a strongly basic *p*H reading, with concomitant improvement in vulcanizing properties. In Table XV are the rubber compounding results in compound No. 5, using color carbon K.

TABLE XIV

Carbon	Stearic acid	Optimum vulcanization at 260° F.	Modulus	Tensile strength
N	0	25 min.	650	4100
N	4	30 "	700	4600
P	0	30 "	750	3200
P	4	40 "	975	4500

Notes:
(1) Without the addition of fat acids both carbons showed quick but poor vulcanization.
(2) The low *p*H carbon suffered much more severely from the lack of fat acid than did the higher *p*H carbon.
(3) The addition 4% stearic acid improved both carbons but the low *p*H much more so than the high *p*H. In both cases vulcanization, although apparently retarded, was actually developed.
(4) In general, the relationships with Tuads were similar to those with merceptobenzothiazole.

TABLE XV

Carbon	Optimum vulcanization at 288° F.	Modulus	Tensile strength	Tensile product
K	45 min.	575	3300	225
K Deactivated	35 "	925	4450	300

III. THEORETICAL CONSIDERATIONS

Significance of pH *Properties.*

The *p*H properties of colloidal carbon have recently been the subject of a communication[15]. The following constitutes a summary of those features believed most relevant to vulcanizing behavior. The inherent surface of carbon is believed to be selectively adsorptive towards hydrogen ions. In proportion as combined oxygen, in the form of what has been termed the C_xO_y complex, becomes attached to the surface, this tendency is reversed. In both cases the ability to affect the glass electrode on the *p*H electrometer and the vehicles in which carbons are customarily used depends on the development of sufficient surface or fineness of subdivision. If the carbon particles are smaller than about 0.2 micron in diameter, these conditions are fulfilled and *p*H values are recorded ranging from 11 to 3 in a continuous series.

In the presence of water the basic carbon particles are surrounded by an outer layer or atmosphere of hydroxyl ions, and in the case of acid carbons by an atmosphere of hydrogen ions. In both cases these ions are sufficiently active to influence the glass electrode, but in neither case is there any development of free

extractable acid or base. However, in the presence of neutral salt solutions, both basic and acid *p*H carbons are able, by hydrolytic adsorption, to release the corresponding base or acid in free form.

In a pigmented rubber system adsorptive forces become operative, and these are controlled as to direction and intensity by *p*H properties, and as to amount by the additional factor of particle size or specific surface. Two independent variables are therefore present and require analysis in order that the vulcanizing behavior of colloidal carbon, in any given system, can be understood and so controlled.

The preferential adsorption of acid carbons for basic materials is now recognized as an important factor in the retardation of the drying of paints. In Table XVI are shown the comparative adsorption characteristics of carbons L, P, J and Q for cobalt, manganese and lead from their naphthenate solutions in petroleum solvents[16]. These metals are commonly used as paint driers and the differences, which are marked, are to be ascribed to the combined action of *p*H and of particle size.

Table XVI

Adsorption of Metal Naphthenates by Carbons from Petroleum Solvent

Carbon	Parts as metal adsorbed per 100 parts carbon		
	Cobalt*	Manganese*	Lead†
L	0.8	0.9	3.0
P	1.2	1.4	5.3
J	2.6	2.6	11.6
Q	4.3	3.9	21.0

* End concentration in solution 0.05 parts per 100 of solution.
† " " " " 0.50 " " " " "

Table XVII

Adsorption of Zinc Laurate by Colloidal Carbons from Benzene Solution

Carbon	Parts zinc as metal adsorbed by 100 parts carbon
L	0.3
P	0.5

A similar adsorptive behavior towards soluble zinc seemed probable, and in Table XVII are shown values obtained in these laboratories for zinc laurate adsorbed from 0.7% solutions in benzene by carbons L and P[17]. It will be seen that carbon P shows an increased capacity for zinc removal, closely paralleling its behavior with cobalt, manganese and lead. The next step was to attempt an order of magnitude calculation as to the corresponding requirements of the same carbons for zinc dissolved in rubber. This was done with two assumptions as regards zinc left in solution in the rubber, first, for an estimated minimum residuum of 0.25% zinc and, second, for a residuum of 0.8%, in both cases quantities being calculated to 100 parts of rubber, and for a 50% carbon tread.

The results shown in Table XVIII, subject to the reservations indicated, supplied theoretical zinc oxide requirements for comparison with rubber compounding and vulcanizing data.

In addition to adsorption of zinc, there are also to be taken into consideration the adsorptive capacities of various carbons for accelerators.

The measure of this tendency, in respect of D.P.G., is the so-called X value which is influenced both by *p*H and particle size[15]. These X values, together with *p*H, are shown in Table I.

The data of sections I and II will now be reviewed.

Rubber-Sulfur Compounds.

The fact that without exception carbon blacks ranging from the ultra rubber type to the finest particle color blacks, and varying in *p*H from 5.5 to 3.1, all accelerated vulcanization as determined by physical properties, coupled with the fact that this accelerating tendency did not run parallel either to *p*H or to particle size, suggests that we may here be dealing with a phenomenon in which vulcanization and reinforcement are interrelated[18].

The effect of selective adsorption in the removal of naturally occurring accelerators or of naturally occurring fat acids must for the same reason be discarded as

TABLE XVIII

THEORETICAL ADSORPTIVE REQUIREMENTS OF CARBONS FOR SOLUBLE ZINC IN 50% MERCAPTOBENZOTHIAZOLE TREAD

(All values on 100 rubber)

Carbon	*p*H	ZnO adsorbed for 0.25% left in soln.	Corresponding total ZnO required	ZnO adsorbed for 0.8% left in soln.	Corresponding total ZnO required
L	4.8	0.3	0.6	0.5	1.3
P	3.8	0.6	0.9	0.9	1.7

Note:
Above calculations involve the following assumptions:

(1) Adsorption from rubber equals adsorption from benzene.
(2) Adsorption isotherm of Zn has same trend as isotherm for cobalt.
(3) No compensation made for hydrolytic adsorption.

They are therefore only "order of magnitude" values.

a prime factor in carbon acceleration. This accelerating behavior of colloidal carbon is being made the subject of further study in these laboratories.

The accelerating effect of zinc stearate on the unpigmented mixing can be explained by the activating effect on the naturally occurring accelerators. The fact that this acceleration is less marked in the case of the carbon mixings can be ascribed to the adsorptive removal of soluble zinc by the carbon. It is interesting to note that, even in the presence of zinc stearate, carbons L and Q vulcanized more quickly than the pure gum mixing, and carbon J had approximately the same time of vulcanization. The accelerating effect of the colloidal carbon, *per se*, prevailed over the depressing effect of the carbon of the zinc activation effect.

The coexistence of organic accelerators and the carbon accelerator leads to adsorptive disturbances which are no doubt responsible for the prevailing opinion that carbons are retarders of vulcanization.

Diphenylguanidine and Basic Accelerators.

Disturbances of D.P.G. vulcanization may occur either by adsorptive removal of the accelerator or by removal of the activating zinc oxide. The fact that, as seen in Figure 2, carbons with *p*H readings higher than 7 actually accelerate D.P.G. mixings represents the sum of the natural accelerating tendency of the carbon, and a tendency to adsorb zinc and accelerator. To this may be added the possibility that, by hydrolytic adsorption, basic or high *p*H carbons are

capable of splitting any neutral salts present in the rubber compound (such as sodium chloride) with release of free hydroxyl ions, which in turn would tend to accelerate.

Turning now to carbons on the acid side with *p*H of 5 or less, we may expect interference with the D.P.G. vulcanization in two stages: first, the removal of accelerator as being more basic, the immediate effect being retardation; second, in the case of still lower *p*H carbons the removal of soluble zinc, the result of which, by interference with the activation reaction, would be to bring about not only retardation of vulcanization but also deterioration of quality. Fat acid requirements in D.P.G. treads will on this view depend on the extent to which the carbon has depleted soluble zinc. With standard carbons (*p*H 4 to 5) the slight removal of zinc can be corrected by minimal additions of fat acid (1 to 2% on the rubber) and larger additions play no constructive role but, on the contrary, dilute and depress physical properties. On the other hand, with low *p*H carbons (3 to 4) the addition of 4% stearic acid was found necessary to correct the deficiency in soluble zinc, with resulting improvement both as regards quality and rate of vulcanization.

Litharge.

That the effectiveness of litharge as an accelerator depends on its being present in soluble form is well established. The adsorptive capacity for various carbons

Table XIX

Carbon	*p*H	% mercaptobenzothiazole adsorbed from 0.01 normal solution in alcohol
N	4.5	14.4
A	11.2	18.9

in respect of lead soaps, shown in Table XVI, explains the poor vulcanization resulting in litharge compounds which contain only the natural fat acid present in the rubber. The finer the particle size and the lower the *p*H of the carbon, the more marked will be this effect.

Conversely, all carbons can be brought to a vulcanization satisfactory both as to rate and quality through the addition of increasing amounts of soluble lead by way of increased fat acid dosages, to correspond with the total requirements of the carbon, as determined by its *p*H and particle size.

In litharge compounds where accelerator and activator are identical and present in excess, the provision of lead soap in amount sufficient for the adsorptive requirements of the most diverse carbons corrects all disturbing factors, with the result that litharge compounds are unequalled in the elimination of vulcanizing differences throughout the whole range of carbon pigments.

Although least sensitive to carbon differences, litharge compounds are, for the reason mentioned above, exceedingly sensitive to any deficiency in fat acid.

Mercaptobenzothiazole and Acid Accelerators.

In mercaptobenzothiazole compounds, adsorption relationships are quite different from those obtaining in the case of litharge or diphenylguanidine. Acid carbons which adsorb more D.P.G. than basic carbons of similar particle size adsorb less mercaptobenzothiazole than do basic carbons, as shown in Table XIX.

If accelerator adsorption were the controlling factor, high *p*H carbons would retard vulcanization in mercaptobenzothiazole compounds more than do low *p*H

carbons. Since this is not the case the situation as regards soluble zinc becomes most important, and this for two reasons. In the first place the acidic carbon now selectively adsorbs zinc, and in the second place the requirements of soluble zinc are greater. To the amount adsorbed by the carbon, there is needed the additional amount to form the zinc salt of the accelerator. A residuum of zinc oxide is required for vulcanization activation, and to neutralize any free fat acid developed by hydrolytic adsorption (carbon) or chemical reaction (accelerator)[19].

The problem of proper zinc and fat acid balance for mercaptobenzothiazole tread compounds has been approached from two angles: first, the determination of fat acid requirements in the presence of excess of zinc, and second, the determination of zinc requirements in the presence of normal fat acid content. The facts clearly show that a deficiency either in zinc or in fat acid depress mercaptobenzothiazole vulcanization through shortage in soluble zinc. An excess of either ingredient will not compensate for a deficiency in the other[20]. With respect to its reaction to excess fat acid, mercaptobenzothiazole is more like litharge than like diphenylguanidine in that, unlike the basic accelerators which are sensitive to excess of fat acid, mercaptobenzothiazole is sensitive to shortage.

Soluble Zinc Requirements and the Monolayer Theory.

Experiments on the adsorption of zinc laurate from benzene solution (Tables XVII and XVIII) have been made the basis for a rough calculation as to total addition of zinc oxide required on the assumption that a residuum of 0.8% of zinc in solution in the rubber is essential for vulcanization activation. The value for carbon L was 1.3% (on the rubber) and for carbon P, 1.7%. These calculated values are in general agreement with the minimum zinc requirements for proper vulcanization development with the same carbons (Fig. 5). The possibility that carbon reinforcement of rubber is best promoted when there is present a monolayer of stearic acid surrounding each carbon particle has found support[21, 22]. The monolayer requirements for carbons of varying particle size[22] indicate for standard rubber carbons[23] a stearic acid dosage of approximately 10% by weight on the carbon, and these proportions rise to over 30% in the case of high color carbons.

Now, if the further assumption be made that the adsorptive requirements of a low pH rubber carbon (P) will be satisfied when it is surrounded by a monomolecular layer not of stearic acid but of zinc stearate, a simple calculation reveals that for a 10% fat acid dosage the corresponding zinc oxide content will be 1.4% by weight on the carbon or 0.7% by weight on the rubber in a 50% carbon tread.

The fair agreement between this value and the value (0.9) derived from direct adsorption experiments (Table XVIII) and from the empirical requirements as revealed in Figure 5 would seem, as a first approximation, to support the view that the vulcanizing behavior of acidic rubber carbons is likely to be most satisfactory when fat acid and zinc are present in amounts required for the development of the above-mentioned monolayer of zinc stearate, plus of course a residuum for vulcanization activation.

For any given particle size of carbon, ideal monolayer disposition presupposes strong attractive forces between carbon and zinc, and is thus dependent on low pH. A decrease in these attractive forces, as represented by higher pH values, would be expected to show a progressive diminution in the density of packing of the zinc stearate molecules.

When the pH of the carbon rises above the neutral point the necessity for a bridge between carbon and the carboxyl end of the fat acid molecule will dis-

appear, and a satisfactory reinforcement bond can be pictured with the hydrocarbon end of the fat acid attached to the rubber, and its carboxyl end attached to the basic (high *p*H) carbon surface.

Empirical Approach to Zinc, Fat Acid, and Accelerator Balance.

Owing to the fact that *p*H and particle size are independent variables, offering many combinations, blanket rules are impossible of formulation. Each carbon presents an individual colloidal adsorption picture. Any change, either in its *p*H or in its particle size, offers in turn a fresh compounding problem.

As a first step, it is suggested that with zinc oxide present in excess (5%), fat acid dosage be systematically varied to optimum properties. A slight excess must be added to allow for crude rubber variability. With fat acid thus determined, zinc oxide may gradually be reduced to the point beyond which the physical properties of the vulcanized rubber begin to suffer. Additional zinc oxide should then be added to allow for variation in carbon or other ingredients. Lastly, accelerator dosage should be adjusted to practical requirements of vulcanization rate, antioxidant effect, and so on. It is believed that such a sequence will best bring out the vulcanizing properties of colloidal carbons at minimum expense.

Where pine tar is used as softener or dispersing agent, its acid characteristics should be taken into consideration during the adjustment of fat acid content.

SUMMARY AND CONCLUSIONS

1. Experiments with rubber-sulfur mixings showed that colloidal carbons accelerated vulcanization instead, as generally stated in the literature, of retarding. The fact that this acceleration was found to be independent of the *p*H value of the carbon suggests that the carbon rubber reinforcement "reaction" and (physical) vulcanization may be related phenomena.

2. When colloidal carbon is used, as in tire treads, in conjunction with other accelerators, disturbances occur due to the selective adsorption properties of the carbon colloid. These disturbances, which are greatest with basic organic accelerators, less with acidic organic accelerators, and least with inorganic accelerators such as litharge, have led to the description of colloidal carbons as quick-or-slow-vulcanizing.

3. The best guide to this "rate of vulcanization" characteristic of rubber carbons is their *p*H value.

4. Adsorption data are given for cobalt, manganese, lead and zinc soaps, and vary widely for different colloidal carbons. This variation as to the zinc requirements was confirmed by a rubber compounding series. Thus each carbon, depending on its *p*H and particle size, presents an individual problem in adsorptive requirements, involving fat acid, zinc oxide and accelerator, which should be adjusted in this order.

5. For use with basic accelerators, *e.g.*, D.P.G., colloidal carbons of maximum surface (which involves high fat acid additions with resultant interference with the accelerator) or carbons with low *p*H (which requires high soluble zinc and therefore high fat acid) are not recommended. Low *p*H carbons tend to disturb the alkalinity essential to best results, and to adsorb the accelerator.

6. With acid accelerators, *e.g.*, mercaptobenzthiazole, the finer colloidal carbons of moderate to low *pH* may safely be used. The higher fat acid dosage (soluble zinc) which these carbons require can be freely supplied, since it does not deactivate the accelerator.

7. For use with litharge, the widest range of colloidal carbons is permissible, extending even to the finest particle high color carbons of pH 3, provided fat acid (and, therefore, soluble lead) is present in amount sufficient for the pH and surface requirements in each case.

8. The possible development and implications of mono-molecular zinc soap layers on colloidal carbon are briefly discussed.

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DIELECTRIC MEASUREMENTS IN THE STUDY OF CARBON BLACK AND ZINC OXIDE DISPERSION IN RUBBER *

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INTRODUCTION

There exists a need for improved methods in the study of dispersion in rubber of such pigments as carbon black or zinc oxide. Furthermore, many of the physical tests used in evaluating rubber compounds are not sensitive measures for differentiating between rubber compounds containing channel process carbon blacks from different sources, although these blacks may differ from one another in chemical and physical properties. It was thought that a more sensitive test for determining differences in carbon black rubber compounds would be obtained by studying their dielectric properties.

A recent survey of the literature indicates that a systematic investigation has not been published of the effect on dielectric properties of rubber when various types of zinc oxide or carbon pigments have been added to the rubber. Apparently a difference in opinion exists also regarding the effect of carbon black on the dielectric properties of rubber.

The work herein reported was carried out to determine the influence of some of the types of zinc oxides and carbon blacks now used in rubber on the dielectric constant, power factor, conductivity and d.c. resistivity of rubber compounds containing various amounts of these pigments.

It was hoped that these data would show whether or not dielectric measurements could be made the means of studying the nature of dispersion in rubber of various types of pigments.

The first published data on the effect of volume loading of zinc oxide on the dielectric properties of rubber was by Curtis and McPherson[1]. These investigators, however, limited their study to one zinc oxide of undisclosed composition and particle size. Williams and Kemp[2] studied the effect of pure French process zinc oxide on the water absorption and dielectric stability of rubber compounds, and concluded that zinc oxide was an excellent pigment for use in soft rubber insulation.

Curtis and McPherson[1] were also the first to study the effect on the dielectric properties of rubber of the addition of a fine particle size carbon black. They found that the addition of 10% carbon black to a pure gum compound adversely affected its dielectric properties. A measurable effect was found when only 2% black was added. Dunsheath[3] found that the addition of 10 parts of a lamp black to 100 parts of rubber doubled its power factor, and that 10 parts of a carbon black quadrupled it. On the other hand, Wiegand and Boggs[4] report that the addition of properly made and dried carbon black up to 10 parts by weight on 100 parts of the rubber hydrocarbon in rubber-insulating compounds results in marked improvement in the dielectric strength, resistivity, and power

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 17, pages 893-909.

factor, without serious increase in dielectric constant. The carbon black employed by them was Micronex, which had been heated 2 hours at 166° C. before it was added to the rubber.

MATERIALS TESTED

Zinc Oxide Compounds.

In the zinc oxide series of tests the following base compound was employed:

ZINC OXIDE BASE COMPOUND

Pale crepe	100.00	parts by weight
Stearic acid	1.25	
Sulfur	3.50	
Diphenylguanidine	0.75	
Di-β-naphthyl-p-phenylenediamine	0.50	
Zinc oxide	5.00	

In addition to the base stock, three compounds were made by adding to it 100, 200 and 300 parts by weight of zinc oxide per 100 parts of base compound. Care was taken to see that the zinc oxides were well dispersed. These compounds were repeated, using the following five different types of zinc oxide:

ZINC OXIDE EMPLOYED

Type	Average particle size†	Water-soluble impurities %
A (French process)	0.12μ	0.01–0.02
B "	0.19μ	0.01–0.02
C "	0.40μ	0.01–0.02
D (American process)	0.35μ	0.32
E "	0.15μ	0.66

† Supplier's data.

A range of vulcanizations was made at 142° C., and the best selected for electrical tests.

Carbon Black Compounds.

The following base compound was employed in the carbon black series of compounds:

CARBON BLACK BASE COMPOUND

Smoked sheet	100.00	parts by weight
Stearic acid	3.30	
Sulfur	2.80	
Mercaptobenzothiazole	0.74	
Zinc oxide	7.80	
	114.64	

The blacks used in this investigation consist of four commercial rubber grade carbon blacks made from natural gas by the channel process, and three commercial rubber grade "soft" blacks made from natural gas by thermal decomposition. The channel process blacks are designated as X-1, X-2, X-3 and X-4. The thermal decomposition process blacks are referred to as Y-1, Y-2 and Y-3.

Two series of tests were made. One series was for comparing poor and normal dispersion of different blacks, using 30 parts by weight with 114.64 parts of the

base compound. The other series was for comparing the effect of various loadings of blacks, using 10, 20, 30, 40 and 50 parts with 114.64 parts of the base compound. A colloidal graphite was included in both series.

Poor and normal dispersion of the different blacks were obtained by varying the milling schedules. To obtain what is designated as poor dispersion a short milling schedule was employed, which resulted in a lumpy dull stock. Normal dispersion was obtained by using a longer milling schedule, and resulting stocks were smooth, glossy and free from evidence of lumpiness.

Vulcanization was carried out in a sheet mould in a press at 137° C. for 60 minutes in the case of the channel process black compounds, and for 45 minutes in the case of the "soft" black rubber compounds. A range of vulcanizations and physical tests were made also to select the proper vulcanization and to study the effect of dispersion and type of black used. These data, however, will not be given, since they are not particularly pertinent to the subject of this paper.

METHODS OF MEASUREMENT

Thickness of Test Specimens.

The test-specimens were in the form of sheets about 13 cm. square. The zinc oxide-filled sheets were approximately 0.12 cm. thick, and the carbon black-filled sheets about 0.24 cm. The thickness was measured with a Schopper micrometer, which could be read to ± 0.0005 cm. At least ten measurements were made in a symmetrical pattern on each sheet within the area covered by the upper electrode.

Electrodes.

The electrodes were cut from tinfoil approximately 0.005 cm. thick. The bottom electrode was cut to cover most of one side of the sheet. The top electrode was cut to a diameter of approximately 10 cm., having an area of about 79 square cm. A guard ring about 1.5 cm. wide was cut to fit around the top electrode, with the smallest possible space between the electrode and the ring to reduce edge effects to a negligible minimum. The electrode dimensions are arbitrary. Those given above were selected to give a reasonable capacitance value, and to fit the brass shield and disc used to connect the upper electrode and guard ring with the bridge. A very thin layer of petrolatum was rubbed on each electrode and guard ring to make the tinfoil adhere to the test sheet and insure good contact. The electrode and guard ring were then rubbed on the sheet, which was placed on a smooth steel plate connected to the bridge. The brass disc was placed on the top electrode with its shield on the guard ring, and these in turn were connected to the bridge. A discussion of tinfoil electrodes is given by Hoch[5].

Alternating Current Measurements.

The alternating current measurements were made with a shielded capacitance-resistance bridge. A simplified schematic circuit of the bridge and electrode connections is illustrated in Fig. 1.

In the case of the rubber sheets having low capacitance-conductance levels, the capacitance was measured to 0.1 micromicrofarad and the conductance to 10^{-10} mho. In the case of the sheets having high capacitance-conductance levels, the capacitance was measured to one micromicrofarad and the conductance to 10^{-7} mho. The power factor, dielectric constant and specific conductance were calculated. When the electrodes were removed from a test sheet and then replaced, the dielectric constant could be redetermined to within 1% and the specific con-

ductance to within 5% for sheets having the low level capacitance-conductance values. The reproducibility was not as good in the case of some of the sheets which had a very high level of capacitance and conductance.

Direct Current Measurements.

The direct current resistance measurements were made by the direct deflection method, with a galvanometer having a current sensitivity of 2×10^{-11} amperes per mm. scale deflection. The circuit consisted of a battery, the test-specimens, a standard megohm resistance and the galvanometer with a shunt. This apparatus is accurate within 5% for normal deflections, but the error may be greater when the deflections are very small or very large.

RESULTS AND DISCUSSION

It can be seen from Figs. 2 to 6, inclusive, that the rubber compounds containing the zinc oxides with the least water-soluble material give the best dielectric

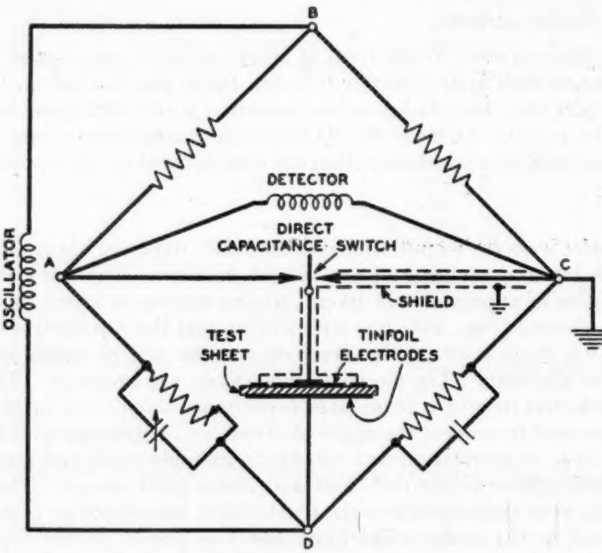

FIG. 1.—Simplified schematic circuit of shielded alternating current bridge and electrode connections.

properties, and that of these the ones of fine particle size in general have less effect on dielectric properties than the coarse. It is apparent also that the adverse effects of water-soluble matter in zinc oxide are increased by the presence of moisture. The adverse effect of water-soluble matter in compounding ingredients on dielectric properties of soft vulcanized rubber has been previously brought out by Williams and Kemp[2]. The zinc oxide causing the highest specific conductance and the lowest specific d.c. resistance in the dry as well as the wet compound has the highest percentage of water-soluble impurities. It is quite evident from these data that investigators should consider the particular type of zinc oxide when studying its effect on the insulation characteristics or water absorption in rubber compounds. The same is undoubtedly true of other mineral compounding ingredients, such as whiting, clays, lithopone, and so on.

The dielectric constants of reinforcing pigments or fillers added to rubber are higher than the dielectric constant of rubber itself, and their addition to rubber should raise its dielectric constant. Lowry[6], however, pointed out that no exact

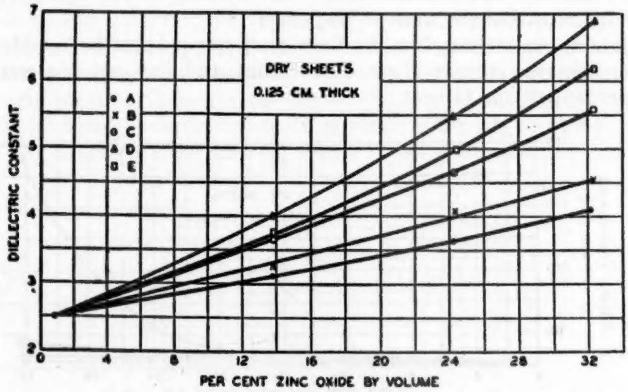

FIG. 2.—Effect of loading on the dielectric constant of zinc oxide-rubber compounds. A to E indicate the types of zinc oxide. The test sheets were dried over phosphorus pentoxide. The measurements were made at a frequency of 1000 cycles per second.

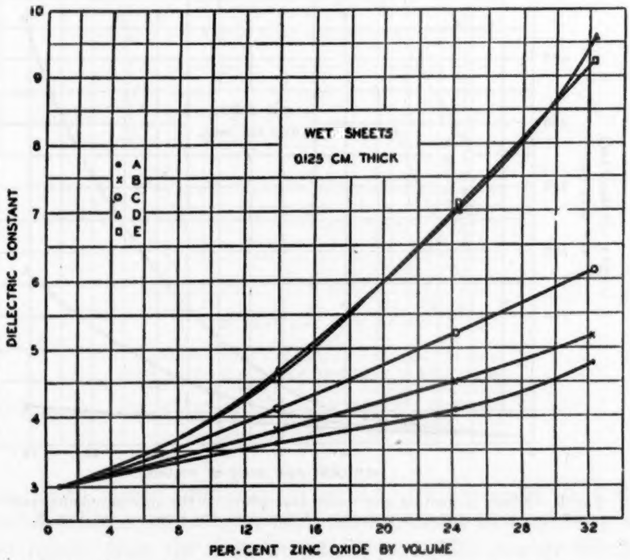

FIG. 3.—Effect of loading and water absorption on the dielectric constant of zinc oxide-rubber compounds. A to E indicate the types of zinc oxide. The dry sheets were immersed in distilled water at 25° C. for 28 days. The measurements were made at a frequency of 1000 cycles per second.

mathematical relationship is known by which one can calculate accurately the dielectric constants of such mixtures from the dielectric constants of the components. This is undoubtedly true, because other factors, such as the size of uniformity of the particles, completeness of dispersion in the rubber, wetability by the

rubber and presence of impurities in the fillers or pigments all operate to affect dielectric properties. If a conducting filler or pigment were dispersed in rubber in such a way as to form conducting paths, it would obviously result in greater changes in dielectric properties than would be the case if an insulating filler, such as calcium carbonate were so dispersed.

Zinc oxide is conducting, but the finer grades appear to be readily wetted by the rubber, whereas coarser fillers, like whiting and clay, are not wetted, as was shown by Schippel[7] and Green[8].

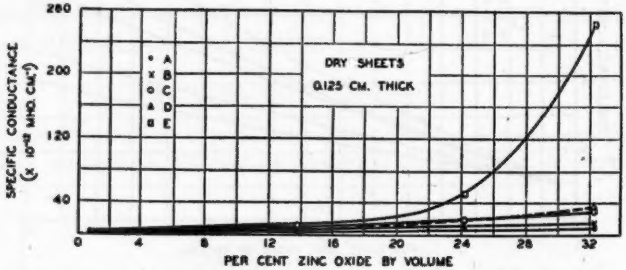

FIG. 4.—Effect of loading on the specific conductance of zinc oxide-rubber compounds. Conditions the same as for Fig. 2.

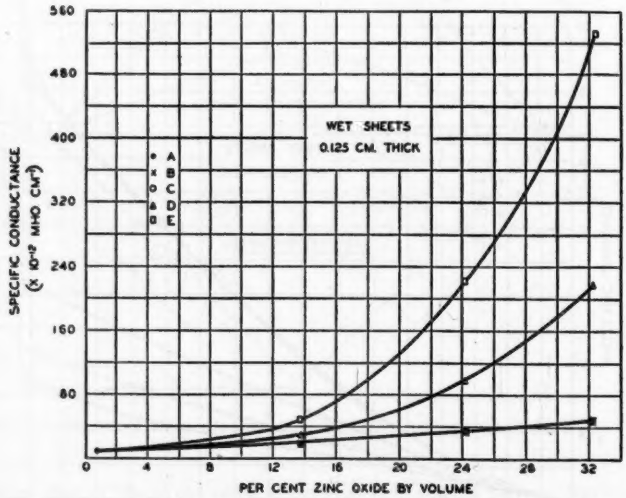

FIG. 5.—Effect of loading and water absorption on the specific conductance of zinc oxide-rubber compounds. Conditions the same as for Fig. 3.

The average diameters of rubber carbons range from about 2 microns for a "soft" black produced by thermal decomposition, to about 0.05 micron for channel process black. The black designated as Y-1 is of the first type with an average particle size generally estimated at about 1 micron, whereas X-3 represents a channel process rubber black with an average particle size variously estimated at from 0.1 to 0.05 micron. Thermal decomposition blacks, Y-2 and Y-3, are of much smaller particle size than Y-1. The graphite employed was the finest colloidal grade obtainable, and probably had an average particle size of the same order as the Y-1 "soft" black.

The above-mentioned carbons were well mixed in the base compound in varying amounts, and dielectric measurements were made on vulcanized sheets of these compounds. The results which are shown in Figs. 7, 8 and 9 are very striking. It will be seen that the effect of the different carbons on the dielectric properties of rubber is widely different, and apparently related to the particle size of the carbon employed. Evidently the finer the particle size of carbon the higher will be the dielectric constant and conductivity, and the lower the resistivity. These effects become more striking for the higher loading of carbon. It will be seen also that the addition of carbon up to 10 parts on 100 parts of rubber in the base compound has relatively little adverse effect on dielectric constant and resistivity

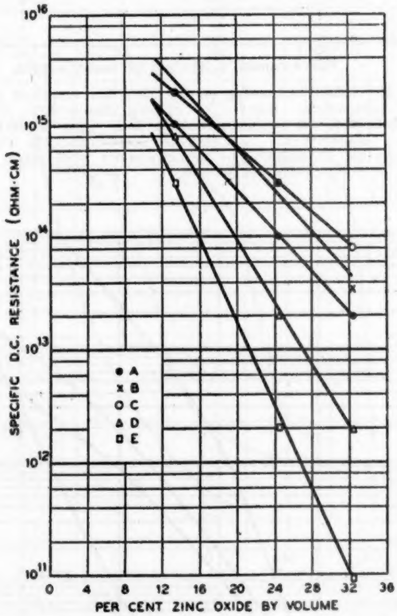

Fig. 6.—Effect of loading and water absorption on the specific d.c. resistance of zinc oxide-rubber compounds. A to E indicate the types of zinc oxide. The dry sheets were immersed in distilled water at 25° C. for 28 days. The measurements were made at 400 volts.

as compared with larger additions. It is indeed unfortunate that the channel process blacks, which contribute the most reinforcement to the rubber, should give the poorest rubber from the dielectric standpoint. The coarser thermal decomposition black and the graphite give relatively low reinforcement, and act more or less like inert fillers in the rubber.

The conductivity and power factor of the rubber are increased by the addition of very small amounts of carbon black, and are much more sensitive than the capacitance or insulation resistance to these additions. It can be seen from Fig. 8 that the addition of 10% of the finer blacks increases the conductivity by about ten-fold. The Y-2 black, which is the finer of the thermal decomposition process blacks, shows a different behaviour from the others. At a 10% loading

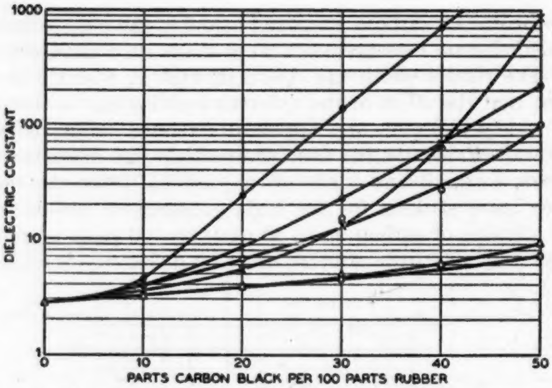

FIG. 7.—Effect of loading on the dielectric constant of carbon-rubber compounds. Key:—○ = channel black X-1. ⊖ = channel black X-2. ● = channel black X-3. □ = thermal decomposition black Y-1. × = thermal decomposition black Y-2. Δ = colloidal graphite. The measurements were made at a frequency of 2000 cycles per second.

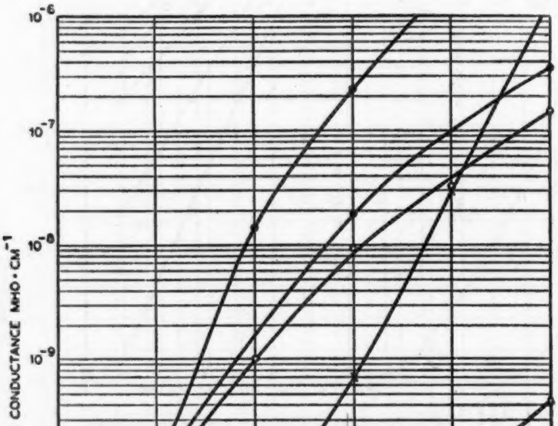

FIG. 8.—Effect of loading on the specific conductance of carbon-rubber compounds. Key the same as for Fig. 7. The measurements were made at a frequency of 2000 cycles per second.

it behaves like the coarser black, whereas at higher loadings it behaves like the channel black.

In our preliminary work we studied the effect of poor dispersion of several blacks, using 50 parts loading on 100 parts of rubber in the base compound. In view of the fact that at this high loading the dielectric properties of the rubber compounds containing the smaller particle size blacks were difficult to measure with satisfactory accuracy, this plan was discarded in favor of employing a 30 parts loading of black in the base compound. The results for the sheets containing 50 parts loading are shown in Table I.

It is seen that the failure to disperse the black thoroughly in the short milling cycle of 8 minutes results in a rubber with better dielectric properties than is the case where the same black is more thoroughly dispersed because of the longer

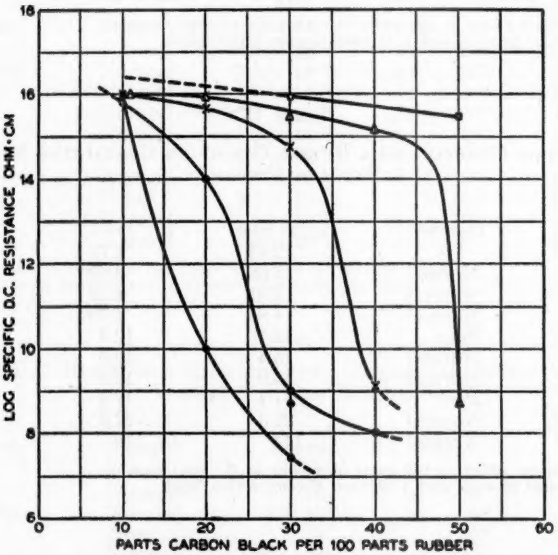

FIG. 9.—Effect of loading on the specific d.c. resistance of carbon-rubber compounds. Key the same as for Fig. 7. The measurements were made at 440 volts.

milling cycle of 15 minutes. This may be explained on the basis that a poor dispersion is somewhat equivalent to employing a black with larger size particles. The same conclusions are reached when one examines the results given in Tables II, III, IV and V, which give the dielectric values for dry and wet sheets containing 30 parts of the different carbons on 100 parts of rubber in the base compound.

The adverse effect on the dielectric properties resulting from water immersion apparently is not very large in the case of sheets containing 30 parts loading of channel black, as seen in Tables II to V. The data in Tables II to VI inclusive show some improvement in dielectric properties, resulting from removal of the initial moisture present in the compounds as made.

To further determine the influence of moisture in the X-3 channel black, it was dried 2 hours at 166° C., as was done by Wiegand and Boggs[4]. It was then compounded with the rubber in amounts of 4.5, 9.0 and 30 parts per 100 parts of rubber in the base formula. The results of dielectric measurements on sheets of these three compounds after vulcanization are given in Table VII.

TABLE I

EFFECT OF DISPERSION ON DIELECTRIC PROPERTIES OF A RUBBER COMPOUND CONTAINING VARIOUS TYPES OF CARBON *

Carbon†	Dispersion	Dielectric constant	Power factor	Specific conductance, mho. cm.$^{-1}$	Specific d.c. resistance, ohm. cm.
Y-1	Poor	7.2	0.023	1.9×10^{-10}	10^{15}
Y-1	Normal	7.3	0.023	1.9×10^{-10}	3×10^{15}
X-1	Poor	69	0.78	9.6×10^{-8}	10^{8}
X-1	Normal	100	0.80	1.5×10^{-7}	6×10^{7}
X-2	Poor	140	0.86	2.7×10^{-7}	10^{7}
X-2	Normal	210	0.84	3.6×10^{-7}	10^{7}
Y-2	Poor	630	0.80	9.4×10^{-7}	$<10^{7}$
Y-2	Normal	910	0.77	1.2×10^{-6}	$<10^{7}$

* 50 parts of carbon added to 100 parts of rubber in the base formula.
† X denotes channel process, and Y thermal decomposition black.

TABLE II

DIELECTRIC CONSTANT OF A RUBBER COMPOUND CONTAINING VARIOUS TYPES OF CARBON *

Carbon†	Dispersion	As made	Dried	After 4 days in distilled water at 25° C.
None	—	2.81	2.77	3.31
Y-1	Normal	4.68	4.62	5.33
Graphite	Normal	4.81	4.72	5.42
Y-3	Normal	4.85	4.79	5.68
X-1	Poor	12.1	12.4	12.8
X-1	Normal	15.4	16.0	16.6
Y-2	Normal	13.0	12.6	14.7
X-2	Poor	17.4	17.5	18.0
X-2	Normal	22.3	22.6	22.7
X-3	Normal	144	119	118

* 80 parts of carbon added to 100 parts of rubber in the base formula.
† X denotes channel process, and Y thermal decomposition black.

TABLE III

POWER FACTOR OF A RUBBER COMPOUND CONTAINING VARIOUS TYPES OF CARBON *

Carbon†	Dispersion	As made	Dried	After 4 days in distilled water at 25° C.
None	—	0.0022	0.0022	0.013
Graphite	Normal	0.0072	0.0057	0.015
Y-1	Normal	0.0075	0.0063	0.014
Y-2	Normal	0.049	0.044	0.056
Y-3	Normal	0.069	0.068	0.076
X-1	Poor	0.31	0.32	0.32
X-1	Normal	0.49	0.49	0.47
X-2	Poor	0.39	0.39	0.38
X-2	Normal	0.59	0.58	0.55
X-3	Normal	0.83	0.69	0.69

* 80 parts of carbon added to 100 parts of rubber in the base formula.
† X denotes channel process, and Y thermal decomposition black.

It is seen that the resistivity is not affected by the addition of 9 parts of this dried black, but that both dielectric constant and conductivity are increased even when 4.5 parts of black are added. These conclusions are not in conformity with those of Wiegand and Boggs, who employed the same type of carbon black, although in a different compound. The small improvement in dielectric properties obtained by these investigators may have been due to the fact that they substituted the black for equivalent volumes of whiting and zinc oxide in heavily loaded stocks. Since the removal of whiting as well as zinc oxide would improve

TABLE IV

SPECIFIC CONDUCTANCE (MHO. CM.$^{-1}$) OF A RUBBER COMPOUND CONTAINING VARIOUS TYPES OF CARBON *

Carbon†	Dispersion	As made	Dried	After 4 days in distilled water at 25° C.
None	—	6.9×10^{-12}	7.0×10^{-12}	4.7×10^{-11}
Graphite	Normal	3.8×10^{-11}	3.0×10^{-11}	9.1×10^{-11}
Y-1	Normal	3.9×10^{-11}	3.2×10^{-11}	8.3×10^{-11}
Y-3	Normal	3.7×10^{-10}	3.6×10^{-10}	4.8×10^{-10}
Y-2	Normal	7.0×10^{-10}	6.1×10^{-10}	9.2×10^{-10}
X-1	Poor	4.4×10^{-9}	4.7×10^{-9}	4.8×10^{-9}
X-1	Normal	9.4×10^{-9}	1.0×10^{-8}	9.8×10^{-9}
X-2	Poor	8.2×10^{-9}	8.2×10^{-9}	8.8×10^{-9}
X-2	Normal	1.8×10^{-8}	1.8×10^{-8}	1.7×10^{-8}
X-3	Normal	2.4×10^{-7}	2.4×10^{-7}	2.3×10^{-7}

* 30 parts of carbon added to 100 parts of rubber in the base formula.
† X denotes channel process, and Y thermal decomposition black.

TABLE V

SPECIFIC D.C. RESISTANCE (OHM. CM.) OF A RUBBER COMPOUND CONTAINING VARIOUS TYPES OF CARBON *

Carbon†	Dispersion	As made	Dried	After 4 days in distilled water at 25° C.
None	—	$>10^{16}$	$>10^{16}$	$>10^{16}$
Y-1	Normal	10^{16}	$>10^{16}$	10^{16}
Graphite	Normal	3×10^{15}	10^{16}	10^{16}
Y-3	Normal	10^{15}	4×10^{15}	10^{15}
Y-2	Normal	7×10^{14}	3×10^{15}	3×10^{14}
X-1	Poor	8×10^{9}	10^{10}	10^{10}
X-1	Normal	10^{9}	10^{9}	10^{9}
X-2	Poor	2×10^{9}	3×10^{9}	3×10^{9}
X-2	Normal	5×10^{8}	8×10^{8}	9×10^{8}
X-3	Normal	2×10^{7}	6×10^{7}	5×10^{7}

* 30 parts of carbon added to 100 parts of rubber in the base formula.
† X denotes channel process, and Y thermal decomposition black.

dielectric properties, the improvement they reported may have been due to the removal of mineral filler, rather than to the addition of carbon black as they assumed.

We have examined also a channel process carbon black recommended for use in rubber insulating compounds which is designated as X-4. In this work this special carbon black was dispersed in small amounts into Paragutta in a Werner and Pfleiderer masticator. Since Paragutta has extremely good dielectric properties it should be possible to determine the effect of small additions of carbon black to it more readily than is the case with rubber. Paragutta is a superior type of thermoplastic insulation developed by these laboratories, which is used for the insulation of submarine cables in place of gutta-percha[9]. It is seen from

Table VI

Dielectric Properties Before and After Drying of a Rubber Compound Containing Various Loadings of a Carbon Black *

Carbon loading	0	10	20	30	40	50
Dielectric constant:						
As made	2.81	4.49	24.8	144	700	2700
Dried†	2.77	4.44	22.6	119	580	1200
Power factor:						
As made	0.0022	0.026	0.47	0.83	0.96	0.82
Dried	0.0022	0.026	0.44	0.69	0.81	0.71
Specific conductance ($mho. cm.^{-1}$):						
As made	6.9×10^{-12}	1.3×10^{-10}	1.5×10^{-8}	2.4×10^{-7}	2.8×10^{-6}	4.3×10^{-6}
Dried	7.0×10^{-12}	1.3×10^{-10}	1.2×10^{-8}	2.4×10^{-7}	8.9×10^{-7}	1.3×10^{-6}
Specific d.c. resistance (ohm. cm.):						
As made	$>10^{16}$	10^{16}	10^{10}	2×10^{7}	$<10^{7}$	$\leq 10^{7}$
Dried	$>10^{16}$	$>10^{16}$	2×10^{10}	6×10^{7}	2×10^{7}	$<10^{7}$

* X-3 black.
† Sheets dried in vacuum at 60° C. for 2 hours.

Table VII

Dielectric Properties of a Rubber Compound Containing Various Loadings of a Dried Carbon Black.*

C.B. loading	Dielectric constant	Power factor	Specific conductance, $mho. cm.^{-1}$	Specific d.c. resistance ohm. cm.
0	2.81	0.0022	6.9×10^{-13}	$>10^{16}$
4.5	3.22	0.0043	1.6×10^{-11}	$>10^{16}$
9.0	4.06	0.018	8.1×10^{-11}	$>10^{16}$
30.0	107	0.80	1.6×10^{-7}	4×10^{7}

* Carbon black X-3 dried for 2 hours at 166° C. before mixing it into compound.

Table VIII

Paragutta Containing Carbon Black

% Carbon black X-4	% Increase in dielectric constant	% Increase in specific conductance	% Increase in power factor	% Decrease in resistivity
0	0	0	0	0
2.5	0	24	24	None*
5.0	6	70	61	None
7.5	22	294	226	None

* Within limit of accuracy of measurement.

Table VIII that additions of as little as 2.5% of carbon black result in a decided increase in the power factor and specific conductance of Paragutta.

The dielectric constant is affected by the addition of 5% black, while the resistivity is unaffected by additions up to 7.5%. It should be possible to detect the effect of adding considerably less than 2.5% of carbon black on the a.c. conductivity of Paragutta. Although in this case the d.c. resistivity was not affected adversely, we obtained no evidence of an improvement in dielectric properties resulting from the addition of small quantities of carbon black.

Black made by the thermal decomposition process is a conducting substance with a particle size of the same order as that of zinc oxide. However, in the case of the channel process blacks, an entirely different situation appears to exist. It is known that the average particle size of channel black is much smaller than that of soft black and of zinc oxide. The additions of channel black result in a greater increase in the modulus and tear-resistance in comparison with what is obtained with zinc oxides or some of the "soft" blacks. The striking change in dielectric properties of rubber resulting from the additions of channel black beyond a certain percentage is, therefore, strong evidence that we are dealing with a different type of dispersion in this case. As long as each particle or group of particles of the carbon black is completely surrounded by rubber, no sharp change in dielectric properties should occur according to dielectric theory. This then leads to the conclusion that a tire tread compound, for example, contains channel black particles, which are so arranged within the rubber phase as to form continuous conducting paths throughout the mass. These paths are more complete when the black is well dispersed, judged from the data herein reported. A poor dispersion of channel black for a given amount should produce less effect on the dielectric constant, since this approaches the situation existing in the case of the blacks having larger particle size. All three channel process blacks, X-1, X-2, and X-3, gave high physical reinforcement of the rubber, irrespective of the fact that in some cases the blacks were poorly dispersed. In the case of sheets containing 50 parts black loading, the tensile strengths for the 60-minute vulcanizations at 137° C. range from 288 to 302 kg. per sq. cm., and the load at 400% elongation varied from 183 to 204 kg. per sq. cm.

In view of these findings, it is concluded that in rubber compounds containing channel black we are dealing with a unique type of dispersion, in which a portion of the carbon black particles are present in the continuous phase, this proportion being larger for the smaller particle blacks. This would seem logical, since the extremely high surface energy and adsorption forces existent in the extremely small channel black particles suggests their possible distribution between the colloidal rubber hydrocarbon units as a true colloid dispersion. This unique type of distribution may account also for the high tear-resistance and modulus of such compounds, since the black would add reinforcement to the colloid structure. It is probable that only a part of the carbon black can be so perfectly dispersed by employing present methods of mixing, whereas the remainder is flocculated. We find, for example, in testing a poorly dispersed channel black compound in direct comparison with the same compound in which the black is well dispersed by more milling, that no appreciable difference exists in such properties as tensile strength, modulus, tear, flexing or abrasion resistance. This may be accounted for on the basis that the gains due to better dispersion of the black are offset by the loss due to the greater breakdown of the rubber. There may be also a limited amount of black of a given particle size capable of being perfectly dispersed, and this limit is approached even after a small amount of working. In these experiments the

poorly dispersed black compound was dull in appearance and definitely lumpy. The well dispersed stock was smooth and glossy in appearance, and the dispersion of the black seemed very good. This is a matter of considerable interest to investigators of tire tread compounds. It should be possible by the electrical method to follow the dispersion of different carbon blacks, or of the same black resulting from different mixing procedures and from variations in minor compounding ingredients. The present authors wish to propose that the dielectric properties be measured and used as a guide, since they appear to be most sensitive to these variations. This statement is based on the conclusion reached from this work that (1) the smaller the particle size and (2) the better the dispersion of a channel process carbon black in a rubber compound, the higher will be its dielectric constant, power factor, and specific conductance and the lower its specific d.c. resistance. One must of course make comparisons only when equal volumes of carbon black are used and when other factors are kept constant. Additions of 30 parts of carbon black to 100 parts of smoked sheet rubber by weight appear to be well suited to bring out the effects desired. The number of other compounding ingredients should be kept to a minimum and as little used as possible. The effects on dielectric properties of the normal variations in relatively small volume of stearic acid, zinc oxide, accelerators and antioxidants used, are small in comparison with the effect of the carbon black. Normal variations in the vulcanization of well-vulcanized specimens will result in little change in the dielectric properties.

Cassie, Jones and Naunton[10] have shown that the power factor of a rubber compound containing carbon black increases with time of vulcanization, especially in the early stages. We have confirmed this, and have found also that the dielectric constant and conductivity increase and the resistivity decreases as the result of vulcanization.

SUMMARY AND CONCLUSIONS

The dielectric constant, power factor, conductivity and d.c. resistivity of rubber compounds containing various types and quantities of zinc oxide and carbon pigments have been measured.

It has been shown that the dielectric properties of rubber compounds having high loadings of zinc oxide depend on the particle size and purity of the zinc oxide used. The French process oxides with the smallest particle size were found superior to other grades. Water-soluble impurities in zinc oxide are shown to have a deleterious effect on dielectric properties, especially in the presence of moisture.

The effect on dielectric properties of adding carbon black to a rubber compound has been shown to be dependent on the type and amount of black added, and on the nature of its dispersion in the rubber.

The dielectric properties of rubber compounds containing "soft" black made by the thermal decomposition process are shown to be distinctly superior to, and widely different from, those of the same compounds containing equal amounts of channel process black.

The general conclusion has been reached that the smaller the particle size and the better the dispersion of carbon pigments in the rubber, the greater will be the increase in the dielectric constant and conductivity, and the greater will be the decrease in resistivity.

The addition of 4.5 parts of a channel black dried at 166° C. to 100 parts of rubber in the base compound increased the dielectric constant and power factor. The addition of this black up to 9 parts did not affect the resistivity. In no case did we find any improvement in the dielectric properties of rubber as a result of

adding carbon black. The addition of as little as 2.5% of a channel process black to Paragutta has been shown to increase its power factor by 24%.

Large differences were found in the effect of adding different channel process blacks to rubber. It was found that the dielectric constant and power factor were higher and the resistivity lower for a compound in which 30 parts of carbon black per 100 parts rubber in the base compound were normally dispersed than for the same compound in which the same amount of black was poorly dispersed. In the case of the 50 parts loading, poor dispersion lowered the dielectric constant, but did not influence the power factor or resistivity to any great extent.

The results show that dielectric measurements can be used to differentiate sharply between different channel process blacks. These results should prove of value to those interested in a further study of carbon black dispersions in rubber as related to reinforcement, since no significant differences in the physical properties of the rubber compounds containing the three different channel process blacks were found.

It is shown also that the specific conductance is the most sensitive measure of the amount, particle size and degree of dispersion of carbon pigments in rubber.

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FATIGUE IN RUBBER. PART II *

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INTRODUCTION

In the earlier part of this work[1] dynamic methods based on the use of a torsion head were employed for the determination of the modulus and frictional losses of rubber, but unfortunately the frequency range employed was small and bore little relation to the frequencies encountered in practice. In view of the fact that rubber is essentially a visco-elastic substance[2] in the region (up to 20% extension) in which it is most frequently employed, there was the possibility that the elastic coefficients of rubber at frequencies of ten per second (car travelling at high speed) or at one hundred and fifty per second (engine mounting) might be different from those at the low frequencies employed in the torsion head apparatus. A new apparatus was therefore designed and used to measure the modulus and resilience of rubber at frequencies up to one thousand cycles per second. The apparatus which is described in this communication is being employed for the following purposes in addition to the use described above:

(1) For detecting changes in rubber due to fatigue. Ordinary measurements of elastic properties under static conditions, as for example with a durometer, are not sensitive to changes due to fatigue, and it was expected that dynamic measurements over a wide range of frequencies would be more susceptible to fatigue. Such proved to be the case. Samples can be cut from the tread of a tire every thousand miles and "concealed" changes of structure detected which cannot be revealed by ordinary testing methods.

(2) To extend our knowledge of the nature of rubber "elasticity" by studying the frequency characteristics of the elastic properties of natural and synthetic rubbers.

(3) To contribute to our knowledge of the mechanism of reinforcement by studying differences between reinforcing ingredients at different frequencies. For example, a comparison of mixes of the same Shore hardness but containing different reinforcing ingredients is being made in relation to the frequency characteristics of their elastic properties. In this way a certain type of characteristic may be found to be associated with developing a particular physical property such as resistance to abrasion.

(4) To study the value of various organic compounds as fatigue inhibitors, especially for use in rubber articles subjected to high frequency distortion.

(5) To study the compounding of natural and synthetic rubber mixes for the construction of engine mountings and other high frequency vibration absorbing systems.

In the work described in this communication the apparatus has been used only for the determination of the elastic properties of the samples and not for actually fatiguing the samples. By increasing the power input by a factor of ten it is possible to induce fatigue in the samples, and this gives another use for the apparatus:

(6) To study continuously the fatiguing of rubber over a wide range of frequencies. This is made possible since the fatiguing apparatus is also the ap-

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paratus being used to determine the modulus and resiliency of the sample being fatigued.

To enable the range of frequencies to reach high values, it was necessary to employ rubber in compression, when the restoring force per unit displacement is higher and hence the natural period which depends on this factor is also greater. The observation of free oscillations of high frequencies would be far too difficult owing to the extremely rapid rate of decay and, furthermore, rubber articles submitted in service to high frequency distortion are usually under compression. It was therefore necessary to carry out all measurements with forced oscillations. Now, it is a well-known fact that the amplitude of this type of oscillation is very small except under the critical condition of resonance, when the frequency of the driving force is equal to that of the natural period of the system.

Under these circumstances, as will be shown later, the amplitude reaches reasonable proportions even at the highest frequencies employed, and is only limited by the internal friction of the medium.

The mechanism for providing these forced oscillations was a specially designed permanent-magnet type loudspeaker unit supplied with alternating current of any desired frequency. The whole system is adjusted to mechanical and electrical resonance by a process analogous to that used in wireless reception, though in our case the response is measured by a gramophone pick-up, amplifier and meter. A direct and accurate reading of the frequency at which resonance occurs is thus obtained, which can be readily converted by calculation into a value for the elastic modulus for the material. A rather more complicated calculation enables one to obtain a value for the viscous resistance and resilience of the material. Thus, it is possible to draw up a table of experimental values for elastic modulus and resilience over a wide range of frequencies. It should be realized also that, unlike the durometer, measurements of hardness made with this apparatus are directional in character.

Since the amplitude of oscillation at any frequency must of necessity in this apparatus be small and since it was desirable to be able to study the elastic properties of the sample over the whole range of its stress-strain curve, the apparatus was so designed that by superimposing the requisite static load the sample could be studied at any selected point on its stress-strain (load-deformation) curve.

THEORY

For simplicity in mathematical treatment a sample of rubber, acted on by an alternating stress, can be replaced by an ideal spring of spring constant s dynes per cm. and viscous resistance proportional to the velocity of displacement, where b dynes per cm. per sec. is the constant of proportionality. Let the moving mass of the system be m g., x is the displacement in cm. and $F \cos pt$ is the alternating stress in dynes, where p is the angular frequency. We can now write down the equation of motion as follows:

$$m \frac{d^2x}{dt^2} + b \frac{dx}{dt} + sx = F \cos pt.$$

The solution of this equation is well known from alternating current problems in electricity, and is given by:

$$x = \frac{F \cos (pt - \theta)}{\sqrt{(s - mp^2)^2 + b^2p^2}}, \text{ where } \tan \theta = \frac{bp}{s - mp^2}.$$

Substituting the conditions for resonance for amplitude, when $p^2=s/m-b^2/2m^2$, this becomes:

$$x_{\max.}=\frac{F\cos(pt-\theta_m)}{b\sqrt{p^2+\frac{b^2}{4m^2}}},\ \text{where}\ \tan\theta_m=\frac{2mp}{b}.$$

In all the cases examined, $b/2mp \ll 1$, so the above expression reduces to:

$$x_{\max.}=\frac{F}{bp}\sin pt\ \ (\text{accuracy}=\tfrac{1}{2}\%) \qquad \text{......Equation 1.}$$

Similarly, an approximate expression is obtained for s

$$s=mp^2\ \ (\text{accuracy } 2\%) \qquad \text{......Equation 2.}$$

It will be seen from an examination of equations 1 and 2, that if $X_{\max.}$ (amplitude of the oscillation $=F/bp$), F, p, and m are measured, values for b and s can be calculated. From these b and s values, one can deduce the resilience and modulus of the test-piece. Let γ be the modulus in dynes per sq cm.; two cylindrical test samples are used of dimensions, R = radius, and $L=R$ thickness.

$$\gamma=\frac{sL}{2\pi R^2}=\frac{s}{2\pi R} \qquad \text{......Equation 3.}$$

Let the resilience $\%=\phi$: the free oscillations of the system under consideration have an amplitude decay factor given by $e^{-bT/2m}$; this factor gives the ratio of two successive amplitudes and when multiplied by 100 gives the resilience in %, according to the usual rubber testing term. T is here the periodic time $2\pi/p$.

$$\text{Hence } \phi=100e^{-\pi b/mp}$$
$$=100e^{-\pi F/sX_{\max.}}\ \ (\text{substituting from 1 and 2})$$
$$\text{......Equation 4.}$$

A complete analysis would enable a value for the absolute viscosity η in poises to be determined from b. An approximate calculation gives:

$$\eta=b/16R \qquad \text{......Equation 5.}$$

Equations 1 to 5 show in a precise manner how, by the simple process of observing the frequency and amplitude at resonance, it is possible to calculate all the important elastic constants of the material. In addition those results can be obtained over a frequency range, by varying m, the moving mass of the system.

Another useful factor can be determined, namely the rate of heat production, H, in watts, due to the conversion of mechanical energy into heat by internal friction.

Rate of heat production H

$$=n\int b\dot{x}\,dx\ \text{ergs per sec., where } n=\frac{p}{2\pi}$$

$$=n\int_0^T \frac{F^2}{b}\cos^2 pt\,dt$$

$$=\frac{F^2}{2b}10^{-7}\ \text{watts}$$

$$=\frac{FpX_{\max}}{2}10^{-7}\ \text{watts} \qquad \text{......Equation 6.}$$

With the apparatus to be described F has a maximum value of 3×10^6 dynes, and b has a value of 5×10^4 for a rubber tread compound at a frequency of 700 cycles per sec. This gives a maximum heat production of 9 watts.

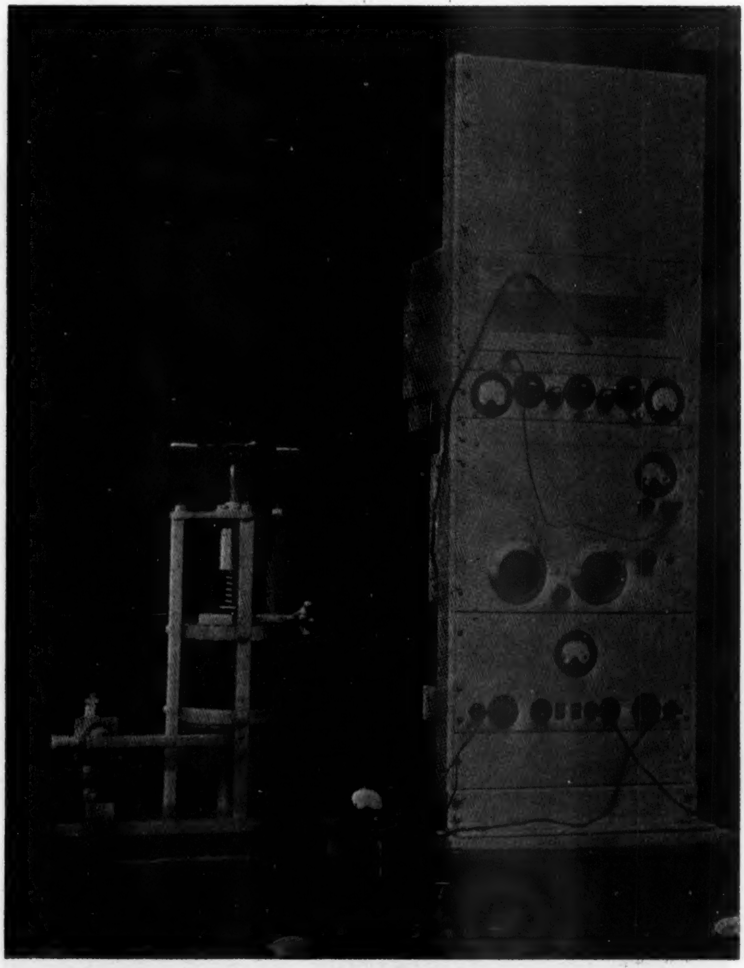

FIG. 1.—Electrical power supply and driving equipment.

APPARATUS

For convenience the apparatus can be divided into three sections:

(1) Electrical power supply.
(2) Driving equipment.
(3) Pick-up and amplifier.

(1) *Electrical Power Supply.*

This is shown in Figure 1—the two middle panels of the rack mounting—and consists of a heterodyne beat oscillator which provides an output of alternating

current of any desired frequency. This alternating voltage is then fed into a power amplifier capable of 30 watts output. The frequency can be continuously varied, so that the "tuning" of the system is simple and the resonant frequency can be read directly off the calibrated dial.

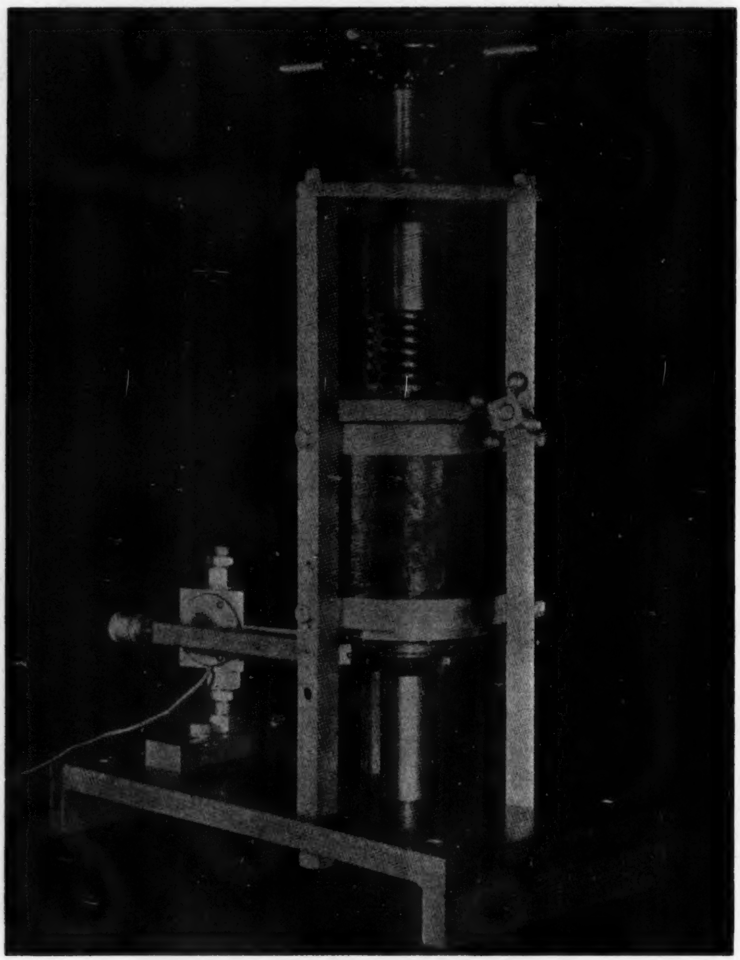

FIG. 2.—Driving equipment.

(2) *Driving Equipment.*

The output from the above power supply is now passed on through a matching transformer to the coil of a permanent-magnet type speaker unit. The general view of this unit is shown in Figure 2. The current and voltage in the driving coil are measured with suitable meters. This enables one to calculate the driving force, once the constants of the magnet are known. Figure 3 shows a close-up of the driving unit and indicates clearly the way in which the alternating stress

is applied to the rubber samples. Two samples are placed on each side of the diaphragm which is attached rigidly to the moving coil. The weight of the diaphragm can be adjusted by a system of pairs of semi-circular rings. In the photograph two semi-circular weights are shown and the other two are removed in order to expose one of the rubber samples; the other rubber sample is hidden from view, as it lies above the diaphragm.

To be able to investigate different parts of the stress-strain curve, static loading up to 2 cwt. can be applied to the top sample of rubber by means of a cali-

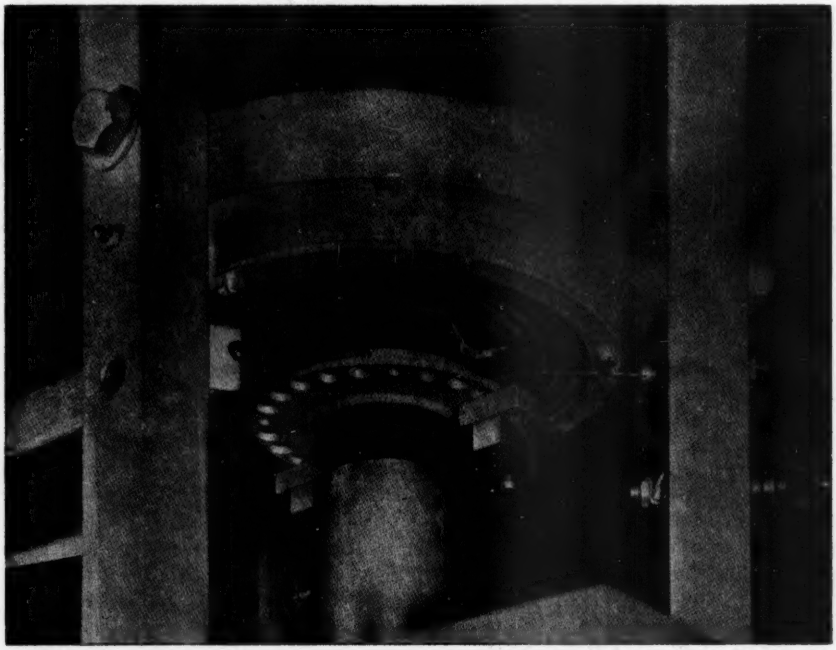

Fig. 3.—Vibrating diaphragm.

brated spring and clamp (see Fig. 2). The whole driving mechanism is very rigidly mounted on a heavy baseplate to avoid any great transmission of the vibration from the rubber samples.

(3) *Pick-up and Amplifier.*

Figure 2 shows the pick-up arm, while Figure 3 indicates how the needle is applied to the diaphragm. When the latter is caused to vibrate an alternating e.m.f. is generated in the pick-up, which is then passed on to the amplifier shown in the bottom panel of the rack mounting in Figure 1. A series of calibration curves enables the e.m.f. readings to be quickly converted into amplitude in cm. These curves can be checked from time to time by observing the vibration with a microscope and micrometer eyepiece.

EXPERIMENTAL

(1) *Mixes.*

For the purpose of a preliminary survey of elastic properties at high frequencies the following mixes were employed:

Soft Rubber

Rubber	100
Zinc oxide	5
Stearic acid	1
Sulfur	2.5
Mercaptobenzothiazole	0.5
Antioxidant	1

Rubber Tread

Rubber	100
Zinc oxide	5
Gas black	40
Stearic acid	4
Sulfur	3
Mercaptobenzothiazole	0.75
Antioxidant	1

Soft Neoprene

Neoprene	100
Magnesia	10
Wood rosin	5
Antioxidant	1
Zinc oxide	5

Neoprene Tread

Neoprene	100
Magnesia	10
Wood rosin	5
Antioxidant	1
Cottonseed oil	5
Gas black	35
Sulfur	1
Zinc oxide	10

The Neoprene compounds were included because of their somewhat different and characteristic elastic properties and because of their outstanding damping characteristics as measured by the tripsometer or by other apparatus[3].

(2) *Conditions of Measurement.*

The maximum static load used corresponds to 2 kg. per sq. cm. The dynamic alternating stress has a maximum value of the same order. It follows that under these maximum conditions a rubber sample is stressed between 0 and 4 kg. per sq. cm. The frequency range investigated is 80 to 500 cycles for a gum mix and 150 to 700 for a tread mix.

(3) *Effect of Time of Vulcanization.*

These measurements were carried out under standard static load (2 kg. per sq. cm.) and with no extra mass attached to the moving diaphragm. Table I gives the figures obtained with a rubber tread mix. In the end four columns are placed together resilience and hardness obtained at high frequency and as obtained on the tripsometer and Shore durometer respectively.

Table I

Vulcanization at 141° C., mins.	Frequency, cycles per sec.	m, g.	$s \times 10^9$, dynes per cm.	$F/X \times 10^8$, dynes per cm.	$\pi F/sX$	Resilience: ϕ H.F., %	Resilience: ϕ Tr., %	Modulus: γ H.F., kg. per sq. cm.	Modulus: S° Shore
0	500	97	1.23	4.58	1.17	31	—	105	35
5	640	—	1.6	2.16	0.424	65	—	136	42
10	660	—	1.7	2.36	0.435	64.5	—	145	50
60	740	—	2.14	2.47	0.36	69.8	64.1	182	62
120	780	—	2.38	2.92	0.384	68	63	202	65

An examination of the Table and Figure 4 shows that with only slight variations the high frequency modulus, H.F., follows the Shore hardness, $S°$, quantitatively. It is quite different with resilience (Fig. 5) since in this case high frequency resilience, ϕ H.F., reaches nearly its maximum value after 5 minutes' vulcanization, whereas tripsometer resilience, ϕ Tr., has a very low value of order of magnitude 50% after vulcanizations as long as 20 minutes. It is highly probable that the falling off of resilience at very short vulcanizations is connected with the effect of mastication, since the resilience of unmasticated raw rubber both by static and dynamic methods is of the same order as that for vulcanized rubber. This is in agreement with the findings and view of Williams[4] that vulcanization does not develop resilience but suppresses plasticity.

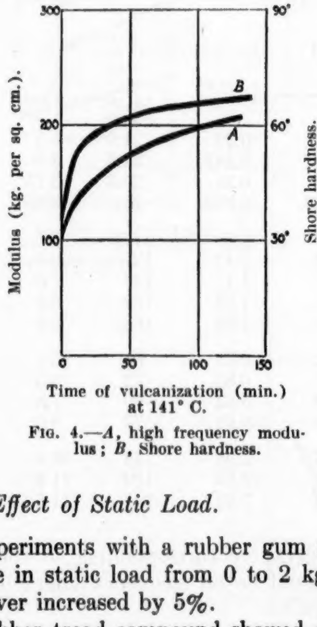

FIG. 4.—*A*, high frequency modulus; *B*, Shore hardness.

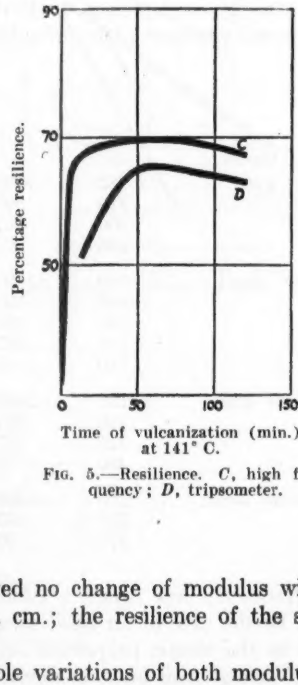

FIG. 5.—Resilience. *C*, high frequency; *D*, tripsometer.

(4) *Effect of Static Load.*

Experiments with a rubber gum mix showed no change of modulus with increase in static load from 0 to 2 kg. per sq. cm.; the resilience of the sample however increased by 5%.

Rubber tread compound showed considerable variations of both modulus and resilience with load, and in addition showed greater changes of hardness with amplitude of vibration. Table II gives some figures to illustrate these points.

TABLE II

Sample	Static load, kg. per sq. cm.	Amplitude, cm. × 10^{-3}	Resonant frequency, cycles per sec.	m, g.	$s \times 10^9$, dynes per cm.	ϕ, %
Rubber tread	0	0.52	210	797	1.38	63
	—	22.2	160	"	0.8	67
	2	1.28	239	"	2.08	76
	—	12.4	215	"	1.72	74
Rubber gum	0	7.0	300	"	0.34	61
	2	8.8	300	"	0.34	66

It will be seen that in both rubber gum and tread mixes, frictional losses are more important near zero strain. This confirms the results previously obtained at low frequencies.

(5) *Effect of Frequency.*

Values for the elastic constants were obtained for the four mixes over a wide range of frequencies, with a static load of 2 kg. per sq. cm. (see Table III).

The last three columns of figures are shown in the accompanying Figures 6 to 8, illustrating the change of elastic properties with frequency. From a study of these curves, the following points can be summarized:

(*a*) In all cases modulus increases with rise in frequency. The extrapolated value at zero frequency correlates well with figures obtained by static loading.

(*b*) Resilience decreases with rise in frequency. The effect of carbon black is the same whether added to rubber or Neoprene, namely, it makes the change with frequency less rapid, a condition more nearly corresponding to the solid state. In the case of an ideal solid there should be no frequency characteristic, as far as the elastic properties are concerned.

TABLE III

Sample	Frequency, cycles per sec.	m, g.	$F/X \times 10^8$, dyne per cm.	$s \times 10^9$, dyne per cm.	γ, kg. per sq. cm.	$b = F/pX \times 10^4$	ϕ, %
Rubber gum	82	1097	0.23	0.29	24.5	4.5	78
	110	597	0.261	0.287	24.2	3.8	75
	200	197	0.34	0.31	26.3	2.75	71
	295	97	0.451	0.332	28	2.45	65
Rubber tread	180	1097	1.07	1.38	117	9.5	78.8
	215	797	1.24	1.42	120	9.1	76
	250	597	1.2	1.47	124	7.6	78
	375	297	1.6	1.64	139	6.8	74
	710	97	2.45	1.93	163	5.5	67
Neoprene gum	130	1097	1.12	0.73	61	13.9	61
	190	597	1.25	0.85	72	10.5	62.5
	325	197	1.58	0.82	69	7.8	54
	490	97	2.73	0.91	77	8.9	40
Neoprene tread	220	1097	2.27	2.06	174	16.4	70.5
	550	197	4.09	2.34	199	11.8	57.5
	875	97	6.34	2.91	247	11.5	50

(*c*) Viscous resistance decreases with rise in frequency. As in the case of resilience, the effect of carbon black is the same whether it is added to rubber or Neoprene. In this case there is an increase in viscous resistance, again corresponding to an approach to the solid state.

It may appear at first sight that the two statements (*b*) and (*c*) are contradictory. On the one hand, resilience decreases with rise in frequency, *i. e.*, a greater percentage of energy is converted into heat; on the other, viscous resistance decreases with rise in frequency. The contradiction is apparent rather than real, since heat development by internal friction depends not only on viscous resistance but also on the velocity of deformation, which is proportional to the frequency. Heat development is, therefore, proportional to bp^2, which actually increases with frequency although b, the viscous resistance, decreases. If only one frequency of deformation is being studied the relative positions of the b curves give accurately an indication of the heat development of different rubbers. This again is true

only for rubbers of the same modulus, since the full mathematical expression for heat development, as shown in the section of this paper devoted to the mathematical analysis, is $\frac{1}{2}Fpx$, which is equal to $\frac{1}{2}bp^2x^2$, where x is the amplitude of distortion.

(6) *Effect of Amplitude.*

The effect of amplitude of oscillations on elastic properties is not very great within the limits studied here. Resilience changes by not more than 2 to 3%,

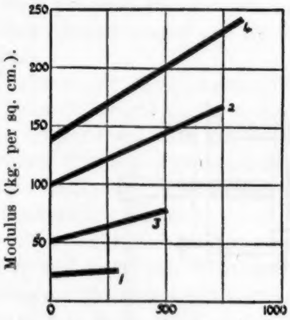

FIG. 6.—*1*, rubber gum; *2*, rubber tread; *3*, Neoprene gum; *4*, Neoprene tread.

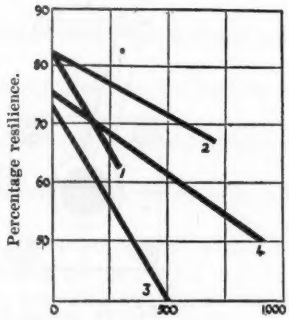

FIG. 7.—*1*, rubber gum; *2*, rubber tread; *3*, Neoprene gum; *4*, Neoprene tread.

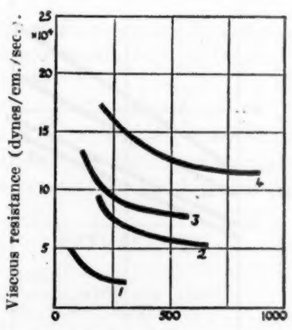

FIG. 8.—*1*, rubber gum; *2*, rubber tread; *3*, Neoprene gum; *4*, Neoprene tread.

which is only just outside the limits of experimental error. Modulus, however, in the case of tread compounds does change appreciably as evidenced by lowering of the resonant frequency by from 5 to 10%. This corresponds to a decrease in modulus by 10 to 20%. It is evident from these data that we are working within but near the elastic limit, where this term denotes the load below which there is complete recovery for practical purposes.

(7) *Effect of Fatigue.*

Pairs of rubber tread samples were fatigued in a special machine (shown in Fig. 9) for different periods of time up to a maximum of 20 hours.

It will be seen from the diagram that a reciprocating arm does work by torsion on two rubber samples under compression.

The rate of cyclical distortion was 200 cycles per minute, or 240,000 cycles in 20 hours. The maximum period of fatigue investigated corresponds to about 500 miles run of a car tire, as far as the number of cycles is concerned, though of course the average distortion is greater than that in a tire running at ordinary speeds. The elastic properties of the samples were tested in the apparatus previously de-

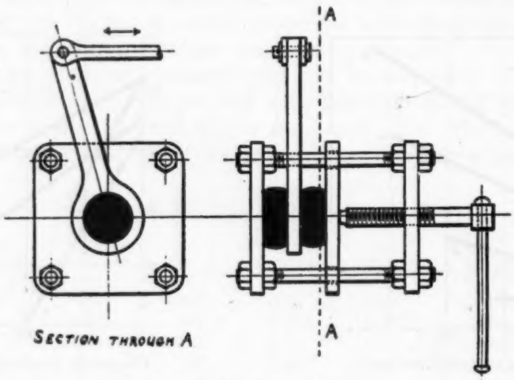

FIG. 9.—Torsion Fatigue apparatus.

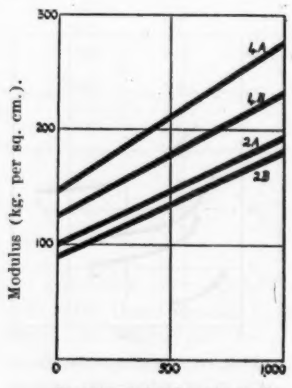

FIG. 10.—*2A*, rubber tread before fatigue; *2B*, rubber tread after fatigue; *4A*, Neoprene tread before fatigue; *4B*, Neoprene tread after fatigue.

scribed, both before and after fatigue. It will be seen from Figure 10 that the product after fatigue is softer than before. This applies over the whole frequency range, including static measurements. In the case of resilience the alteration is greatest at low frequencies: the whole resilience-frequency curve seems to be less steep after fatigue than before; this may be evidence of a tendency to permanent crystallization during working of the rubber. Owing to the experimental difficulties in determining absolute values of resilience, more reliance is placed on the change in modulus.

The softening of rubber under fatigue is of course well known, and has already been reported upon by several other investigators but the softening of Neoprene under fatigue is of great interest, since Neoprene, unlike rubber, tends to harden on aging and hence the softening due to mechanical fatigue will be offset to some extent by the hardening due to chemical deterioration.

SUMMARY

1. An apparatus is described for measuring the modulus and resilience of rubber over a wide range of frequencies.
2. These measurements can be made at any point in the stress-strain curve of the sample.
3. By increasing the power input, the same apparatus can be used to induce high frequency fatigue in the sample.
4. The earlier work with the torsion head apparatus has been confirmed, namely, that internal friction is greatest near zero strain.
5. High frequency resilience is more independent of degree of vulcanization than tripsometer resilience.
6. Modulus tends to increase with frequency. The effect is least with a rubber gum stock and is greater with compounds containing gas black.
7. Resilience decreases with frequency both in gum and gas black compounds. The decrease is more rapid in the gum compounds.
8. Viscous resistance decreases with frequency and becomes constant at higher frequencies.
9. The modulus of both rubber and Neoprene carbon black compounds decreases with fatigue.
10. The change in modulus with frequency in fatigued stocks is exactly analogous to the change before fatigue in rubber, but there is a slight divergence in the case of Neoprene.

In conclusion, the authors wish to express their thanks to Imperial Chemical Industries, Ltd., in whose Rubber Service Laboratories the work was carried out, for permission to publish the results embodied in this paper.

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THE BEHAVIOR OF RUBBER AT LOW TEMPERATURES *

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The behavior of rubber at low temperatures is a question of general interest, the solution of which will not only result in a better understanding of the structure of rubber but will be of great practical importance to aviation and motor transport, as these employ various rubber parts often subject to freezing, which is one of the causes of serious accidents. This question is of special importance to the northern countries which, owing to their geographical situation, have more severe winters, and where mechanical apparatus, airplanes and balloons are therefore obliged to work at lower temperatures than is the case in southern lands. The troubles encountered in aircraft on account of the freezing of rubber gave us the impulse to take up this question. The freezing of raw and vulcanized rubber has been known for a long time, but no quantitative investigations have been made until now, and it was not known at what temperature rubber loses its elastic properties and how and to what degree this is influenced by its composition, etc. The researches of Le Blanc and Kröger[1], Tener, Kingsbury and Holt[2], Kröger[3], Katz[4] and Gibbons, Gerke and Tingey[5] first threw some light on this question and were followed by those of Khvostovskaya and Margaritov[6]; these investigations made it possible to draw certain practical conclusions. Yet the phenomenon is far from being understood. Our work was analogous to the investigations of Khvostovskaya and Margaritov, as it was conducted with a view to its practical application. It must be emphasized, however, that we consider the results obtained only as a contribution to the solution of the problem of the freezing of rubber, for they do not include a complete series of agents having an important influence on this problem. It is intended in future to continue this work. The purpose of the present paper is only to awaken an interest in this problem as being of great importance from a theoretical as well as from a practical point of view.

The apparatus used (Fig. 1A) is a modification of the one used by Khvostovskaya and Margaritov. It consists of a Dewar vessel containing a refrigerating mixture (alcohol plus solid carbon dioxide), a grooved pulley supported by a convenient column, grips for holding the test-pieces, a scale placed on an ebonite rod and a leather cord passing through the groove of the pulley and attached at one end to the ebonite rod and at the other to a plate which can be loaded with suitable weights for the extension of the sample. Rings of an internal diameter of 22 mm., 2 mm. wide and about 1.7 mm. thick, were used for the tests. The test-piece was stretched in the air to a predetermined elongation, which was measured on the scale; the sample was then plunged in the cooling mixture by elevating the Dewar vessel containing the refrigerating mixture. The investigations were conducted at temperatures from -10 to $-70°$ C. The temperature variations did not exceed 1.5° C. during any one measurement, but for the greater part this variation was within about 0.5° C. Since it was ascertained that no difference could be found in the final results whether the time of freezing was 5, 10, 15, 30 or even 45 minutes, 5 minutes was adopted as the average time of freezing. The freezing of the samples was expressed by their permanent set, in relation to

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their initial length, read after the lapse of one minute from the time of releasing the extension weight but without lifting the sample from the cooling liquid. The readings were taken with an accuracy of 0.3 mm. and were recorded in percentages of the semi-circumference of the test-piece, that is, 34.5 mm. The pointer was fixed in such a way that it stood at zero on the scale when the sample was placed in position without tension.

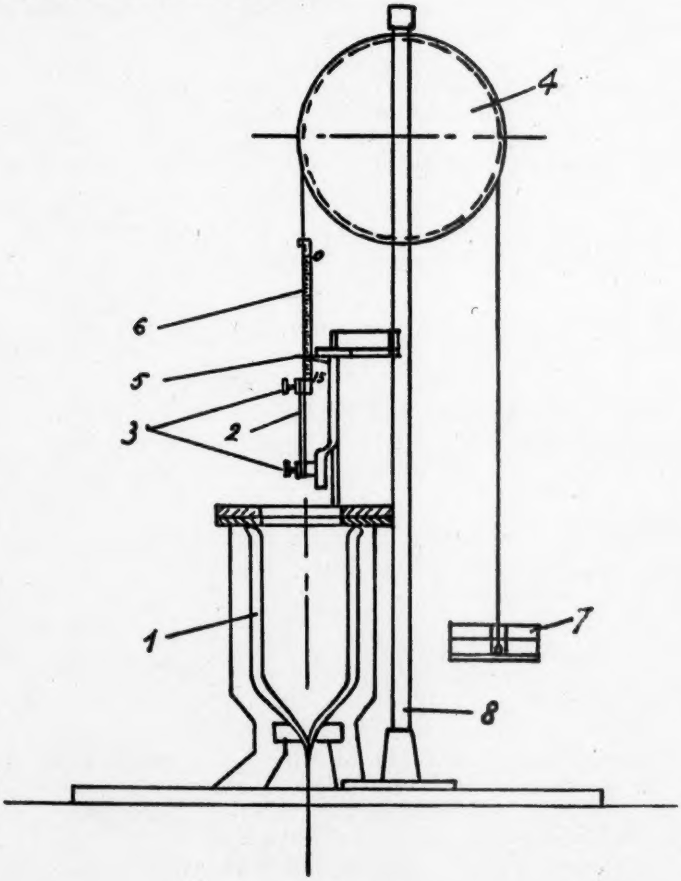

FIG. 1A.

It was decided first to repeat some of the experiments of Khvostovskaya and Margaritov to confirm, by the accumulation of more data, the correctness of their statements in this comparatively new domain.

Two compounds were first prepared, No. 1 and No. 2, the compositions of which were as follows:

COMPOUND No. 1	
Smoked sheet	100.0
Sulfur	4.0
Zinc oxide (White Label)	5.0
Stearic acid	0.5
Vulkacit Mercapto	0.6
Vulkacit Thiuram	0.06

COMPOUND No. 2	
Smoked sheet	100.0
Sulfur	2.5
Zinc oxide (White Label)	5.0
Stearic acid	0.5
Vaseline oil	5.0
Vulkacit P Extra N	1.0

(i) To determine the influence of the elongation of the test-pieces on the phenomenon of freezing, the samples of both compounds, the first vulcanized for 40 minutes at 133° C. and the second for 30 minutes at 110° C., were tested at −40° C. with initial elongations of 25 to 400%. The results (Table I) confirmed the conclusions of the Soviet investigators, namely, that the degree of freezing of rubber increases with increase of elongation, and that this effect becomes very noticeable above an initial elongation of 200%. In the curve for compound No. 2 this sharp increase of freezing above an initial elongation of 200% is distinctly seen (Figure 1).

(ii) To determine the influence of vulcanization on the freezing of rubber, sheets of compound No. 1 were vulcanized at temperatures of 125°, 133°, and 143° C., the rings from these samples being investigated at −40° C. with an initial elongation of 200%. Table II gives the results obtained; there is no evidence of a marked improvement of the resistance to freezing as a result of shortening the time of vulcanization; the Soviet investigators' statement that an increase of the temperature of vulcanization, and therefore a shortening of the time, diminishes the freezing effect has not been confirmed.

Table I

Temperature of cooling, − 40° C.	Comp.	Elongation during cooling (%) 25	50	100	150	200	300	350	400
Permanent set (%).......	1	—	—	—	—	3	14	—	53
	2	0	0.5	3	5	6	35	72	169

Table II

Temp. of cooling, − 40° C. Initial elongation, 200%		Time of vulcanization (minutes) 5	10	15	20	30	35	40	50	60	70	80	100	120
Permanent set (%).	Temperature of vulcanization, 125° C.	—	—	41	—	14	7	—	—	—	—	—	—	—
	Temperature of vulcanization, 133° C.	—	—	—	6	5	—	3	5	6	9	—	—	—
	Temperature of vulcanization, 143° C.	63	19	—	8	6	8	7	8	8	9	11	17	19

(iii) The influence of fillers was investigated with four compounds, which were similar to the base compound No. 1 with the addition of 10 parts by volume of Thermax black, White Label zinc oxide, Arrow gas black and litharge, respectively. Sheets of each of these compounds were vulcanized at 143° C. for 10 to 100 minutes; rings were then cut from the vulcanizates and tested for their resistance to freezing at −40° C., using an elongation of 200%. Table III gives the data for tensile strength and elongation at break as well as the permanent set of test-pieces of the base compound No. 1. Table IV gives the corresponding data for the four compounds with fillers. It is obvious that slight overvulcanization gives for filled rubbers a minimum freezing effect. With a greater elongation this minimum is distinctly shifted into the region of overvulcanization, which again disagrees with the opinion of the Soviet investigators, who found that optimum vulcanization gave the rubber the greatest resistance to freezing.

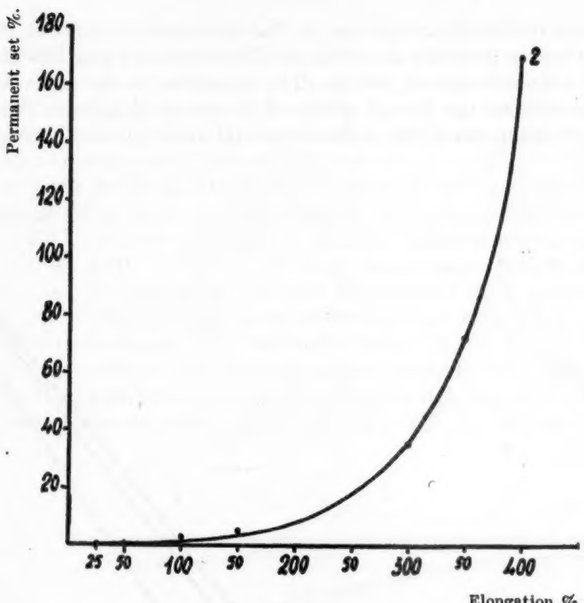

FIG. 1.

TABLE III

Temperature of cooling, − 40° C. Initial elongation, 200%	Time of vulcanization (minutes)				
	20	30	40	60	70
Tensile strength (kg. per sq. cm.)	276	248	262	254	220
Elongation at break (%)	663	671	692	693	680
Permanent set (%)	6	5	3	6	9

TABLE IV

Temperature of cooling, − 40° C. Initial elongation, 200%	Temperature of vulcanization, 143° C.	Time of vulcanization (minutes)							
		10	20	30	40	50	60	80	100
Thermax black	Tensile strength (kg. per sq. cm.)	—	267	261	240	228	207	219	210
	Elongation at break (%)	—	655	650	627	627	616	616	612
	Permanent set (%)	—	12	11	9	9	10	12	13
ZnO	Tensile strength (kg. per sq. cm.)	—	273	267	241	227	233	206	208
	Elongation at break (%)	—	673	666	675	676	679	700	700
	Permanent set (%)	—	19	16	12	13	12	16	15
Arrow black	Tensile strength (kg. per sq. cm.)	—	218	233	220	212	178	162	162
	Elongation at break (%)	—	600	616	603	595	561	543	533
	Permanent set (%)	—	63	53	48	39	35	40	39
PbO	Tensile strength (kg. per sq. cm.)	228	217	215	195	214	—	184	183
	Elongation at break (%)	700	613	600	569	593	—	544	590
	Permanent set (%)	121	76	79	64	76	—	58	70

The purpose of drawing attention to the discrepancy between individual investigators is not to discredit the work of Khvostovskaya and Margaritov, which deserves full acknowledgment, but to draw attention to the difficulty sometimes found in reproducing the results obtained by an investigator. The same compounding ingredients can differ in the shape and dimensions of their particles, the

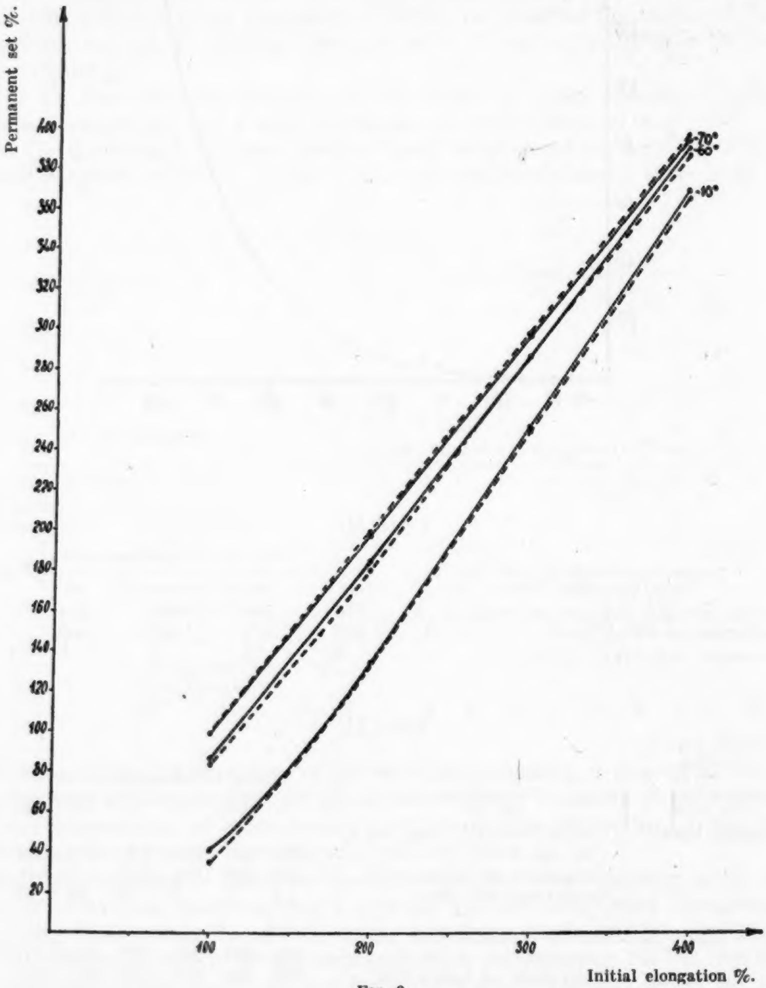

FIG. 2.

quantity of impurities and character of surface, which can influence to a greater or less degree the properties of the compound. The rubber itself may vary also. The first part of our investigation, consisting in repeating certain experiments of the Soviet investigators and clearing up the influence on freezing of the three factors named above, *viz.*, elongation during freezing, temperature of vulcanization and effect of fillers, having been fully dealt with, the original part of our investigation will now be described.

(1) In the first place it was decided to investigate the behavior of raw rubber when cooled, and whether previous heating had any influence on its resistance to freezing. The raw rubber was prepared by placing a sheet of it in a frame of suitable thickness, which was then put in a press heated to 100° C. and kept there for 30 minutes. From the sheet obtained in this way, having a fairly smooth surface, test rings were cut and frozen at temperatures of −10° to −70° C. at initial elongations of 100% to 400%. It will be seen from Table V and Figure 2 that both smoked sheet and crepe freeze to a high degree, but the extent of freezing at −10°, −30°, and −40° C. differs only slightly, a greater difference being observed at or below −60° C. At −70° C. there is an entire loss of elastic properties. To obtain a clearer picture, the permanent set was recalculated as a percentage on the initial elongation to which the test-pieces were subjected while being frozen, instead of on the half-circumference. The results in Table VI and Figure 3 give a clear picture of the behavior of raw rubber at low temperatures. The straight line perpendicular to the ordinate axis and passing through the point 100 represents complete (100%) loss of elastic properties at −70° C. In order to establish

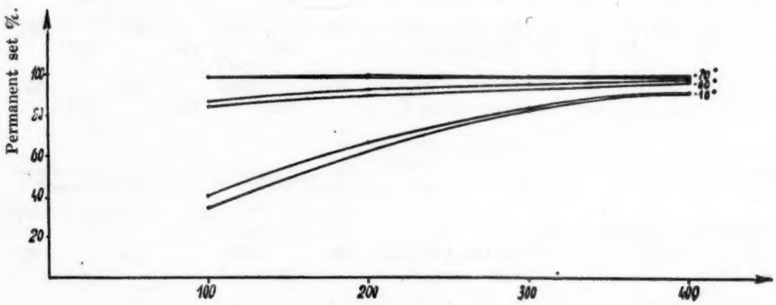

Fig. 3.

whether previous heating of rubber has any influence on its freezing, pieces of smoked sheet were placed in frames of suitable thickness and heated for 30, 60 and 120 minutes at temperatures of 100°, 120° and 140° C.; after 24 hours' recovery test-pieces cut from these sheets were frozen at −40° C. at an initial elongation of 200%. It will be seen from the results presented in Table VII that preheating of rubber even at elevated temperatures has no effect on its freezing. There are small differences between the degree of freezing of a sample heated for 30 minutes at 100° C. and one heated for 60 or 120 minutes at 140° C., but they are negligible and can be considered as lying within the limits of experimental error.

(2) The introduction of softeners into the compound produces—as has been shown by the investigations of various authors—a diminution of internal friction and therefore with certain fillers (oil blacks) an increase of plasticity. Hence arose the question whether the introduction of softeners into rubber will cause a diminution of internal friction at low temperatures and therefore a diminution of freezing. To solve this question several compounds were prepared with pine tar of b.p. 330° to 360° C., Bitupol (petroleum asphalt), vaseline oil and paraffin oil. Compound No. 1 was taken as base compound, and the appropriate softeners were added to the extent of 5 parts by weight per 100 parts of rubber. The permanent set was determined at −40° C., and at an initial elongation of 200%. It will be seen from the results, Table VIII, that the compound containing

Bitupol gave the worst results, whereas there was hardly any difference between the behavior of compounds with the three remaining softeners. On the contrary, with greater initial elongations the behavior of individual softeners is distinctly different. This is illustrated in Table IX, which shows the freezing effects on com-

TABLE V

Temperature of cooling, ° C		% permanent set at initial elongation 100%	200%	300%	400%
—10	Smoked sheet ..	41	134	252	369
	Pale crepe	35	—	250	366
—30	Smoked sheet ..	47	158	264	377
	Pale crepe	40	135	253	375
—40	Smoked sheet ..	49	147	262	368
	Pale crepe	41	133	244	377
—50	Smoked sheet ..	60	167	271	380
	Pale crepe	53	163	268	375
—60	Smoked sheet ..	87	185	287	391
	Pale crepe	84	180	287	388
—70	Smoked sheet ..	99	198	297	395
	Pale crepe	99	199	298	398

TABLE VI

Temperature of cooling, ° C.		% permanent set at initial elongation 100%	200%	300%	400%
—10	Smoked sheet ..	41	67	84	92
	Pale crepe	35	—	83	92
—30	Smoked sheet ..	47	79	88	94
	Pale crepe	40	68	84	94
—40	Smoked sheet ..	49	74	87	92
	Pale crepe	41	67	81	94
—50	Smoked sheet ..	60	84	90	95
	Pale crepe	53	82	89	94
—60	Smoked sheet ..	87	93	96	98
	Pale crepe	84	90	96	97
—70	Smoked sheet ..	99	99	99	99
	Pale crepe	99	100	99	100

TABLE VII

Temperature of cooling, −40° Initial elongation, 200%	Time of heating (minutes) 30			60	120
Temperature, °C.	100	120	140	140	140
Permanent set (%).............	147	149	147	139	126

pounds with the above-mentioned softeners and the base compound studied at −40° C. with initial elongations of 200, 300, and 400%. It will be seen that at an initial elongation of 400% pine tar gives the least freezing. The freezing as compared with that of the base compound is lower. Further investigations on various kinds of raw rubber will establish whether this property of pine tar is always present.

(3) To determine the effect of various quantities of softeners on the freezing of rubber, 5, 10, 15 and 20 parts by weight of vaseline oil were added to compound No. 3.

Compound No. 3

Smoked sheet	100.0
Zinc oxide (White Label)	5.0
Stearic acid	0.5
Sulfur	2.5
Vulkacit P Extra N	1.0

The compounds were vulcanized at 153° C. for 8, 10, 13, 16, 20 and 30 minutes, after which the freezing-resistance of the test-pieces was determined for each degree of vulcanization. Table X contains the lowest results obtained. It will be seen from these that the addition of more than 10 parts of oil by weight causes an increase of the degree of freezing. Further studies with various kinds of softeners must be conducted in order to draw general conclusions.

Table VIII

Temperature of cooling, − 40° C. Initial elongation, 200%	5% based on the weight of smoked sheet	Time of vulcanization (minutes) 10	15	20	30	40	50	60	80	100	180
Permanent set (%)	Pine tar	—	—	9	9	9	10	15	15	—	—
	Bitupol	—	13	13	11	12	14	—	15	—	—
	Paraffin oil	—	—	9	8	8	8	—	—	13	19
	Vaseline oil	18	—	7	10	8	—	10	12	—	—

Table IX

Temperature of cooling, − 40° C.	Elongation (%)	Base compound	Pine tar	Bitupol	Paraffin oil	Vaseline oil
Permanent set (%)	200	3	9	11	8	7
	300	14	16	29	19	21
	400	53	44	77	73	82

Table X

Temperature of cooling, − 40° C.	Elongation (%)	Base compound	Vaseline oil 5 pts.	10 pts.	15 pts.	20 pts.
Permanent set (%)	200	6	6	6	8	9
	300	19	15	16	23	21

(4) To learn more of the characteristics of the phenomenon of freezing, the effects of temperature of freezing and initial elongation were determined for the "pure" rubber compound No. 1. It will be clearly seen from the results presented in Table XI and Figures 4 and 5 that the degree of freezing increases with decrease of temperature; it increases very rapidly between −50° and −60° C. and afterwards more slowly, and at −70° C. there appears to be an entire loss of the elastic properties of the rubber. To render this fact more obvious, the permanent set in Table XI was recalculated as a percentage of the initial elongation at which the test-pieces were frozen, instead of on the half-circumference. The results, given in Table XII and Figures 6 and 7, show more clearly than the preceding ones the effect of temperature on the degree of freezing. Its great increase between −50° and −60° C. is more obvious here, and the straight line perpendicular to the ordinate axis (Fig. 6) indicates a complete (100%) loss of elastic properties at −70° C.

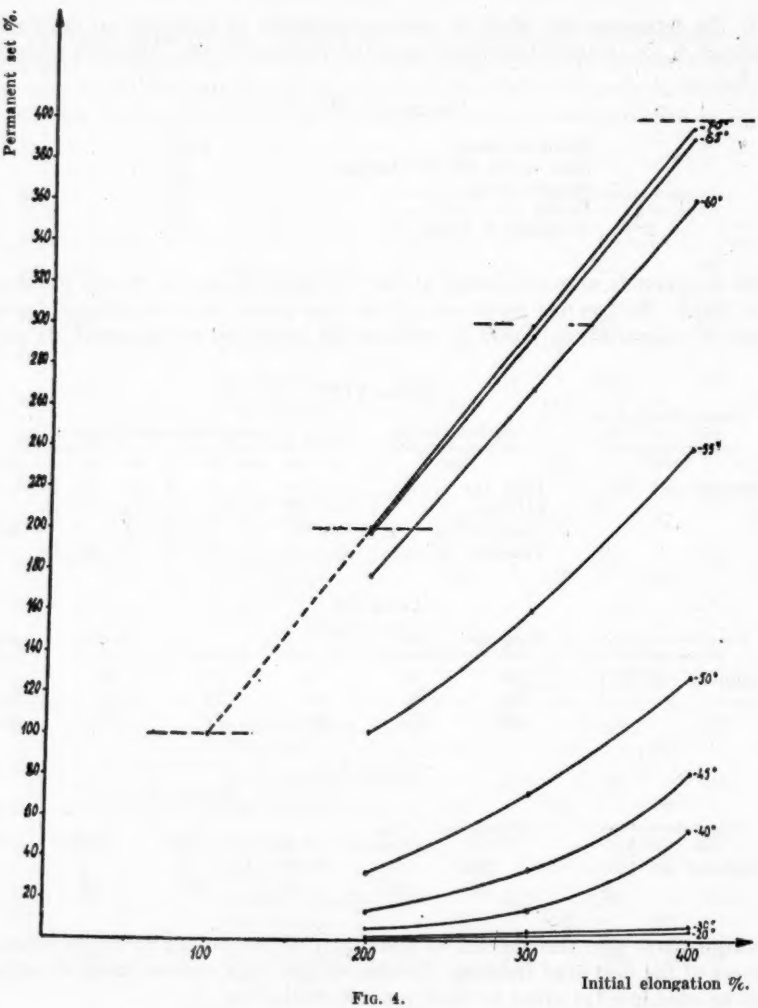

FIG. 4.

TABLE XI

	Elongation (%)	Temperature of cooling, ° C.								
		− 20	− 30	− 40	− 45	− 50	− 55	− 60	− 65	− 70
Permanent set (%).....	200	0.1	1	3	13	32	101	177	198	200
	300	2	4	14	33	71	160	268	295	300
	400	4	6	53	81	128	239	360	391	396

TABLE XII

	Elongation (%)	Temperature of cooling, ° C.								
		− 20	− 30	− 40	− 45	− 50	− 55	− 60	− 65	− 70
Permanent set (%).....	200	0.05	0.5	2.5	6.5	16	51	89	99	100
	300	0.7	1.3	4.7	11	24	53	89	98	100
	400	1	1.5	13	20	32	60	90	98	99

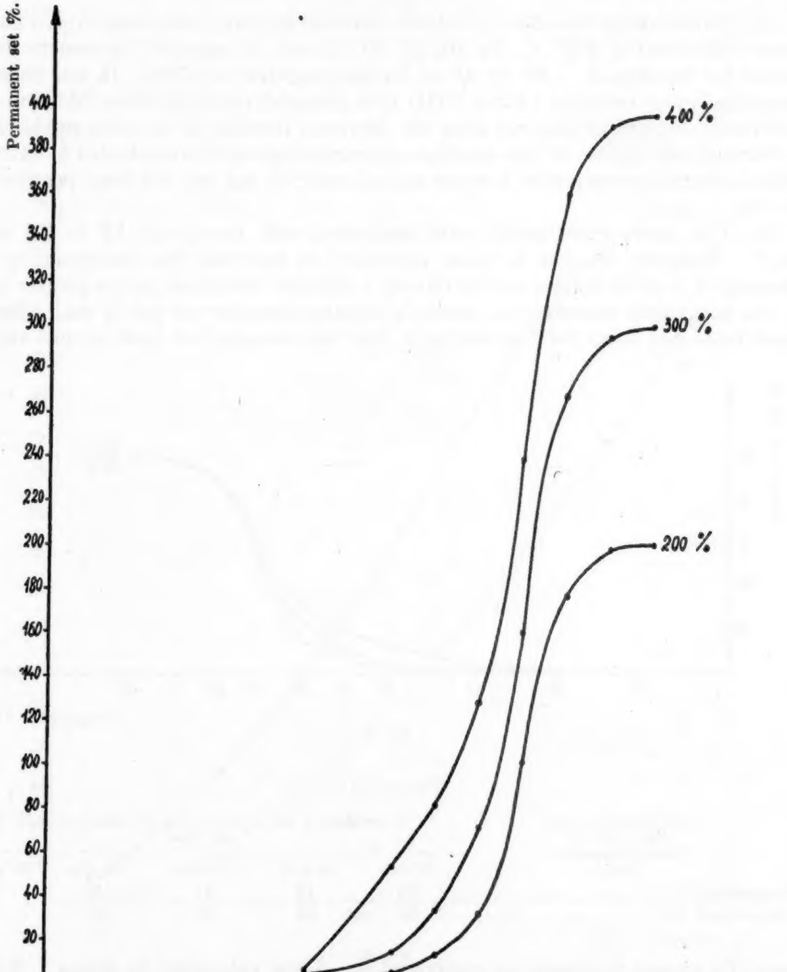
Permanent set %.
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-10
-20
-30
-40
-50
-55
-60
-70
Temp. ° C.
400 %
300 %
200 %

FIG. 5.

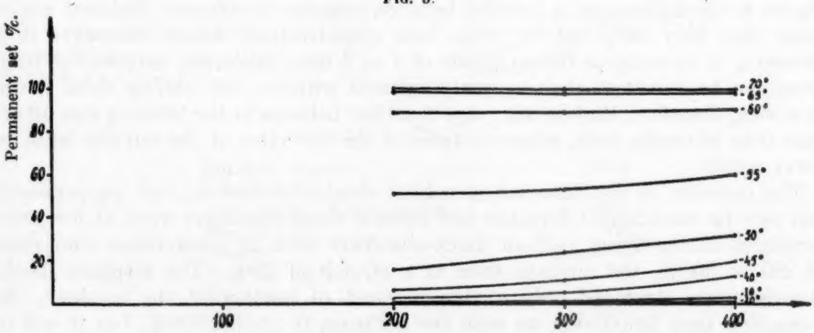
Permanent set %.
100
80
60
40
20
100
200
300
400
Initial elongation %.
-70°
-65°
-60°
-55°
-50°
-45°
-40°

FIG. 6.

(5) To determine the effect of rubber antioxidants, two compounds Nos. 4 and 5 were vulcanized at 143° C. for 10, 15, 20, 25 and 30 minutes; specimens were tested for freezing at −40° C. at an initial elongation of 200%. It will be seen from the figures obtained (Table XIII) that phenyl-β-naphthylamine added under laboratory conditions does not alter the degree of freezing of the compounds. For a thorough elucidation of this question experiments should be conducted at various initial elongations and with various antioxidants; it has not yet been possible to do this.

(6) The above experiments were conducted with test-pieces 1.7 to 2.0 mm. thick. However, since it is often necessary to ascertain the susceptibility to freezing of a given rubber article having a different thickness, say a greater one, it was considered necessary to ascertain whether samples cut out of such objects must be buffed down for this test or if they can be tested at their normal thick-

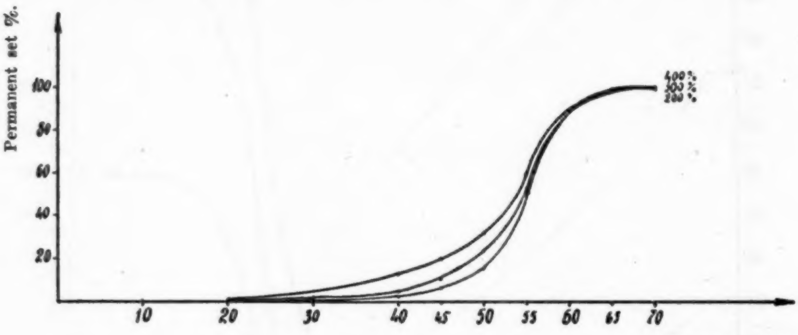

Fig. 7.

Table XIII

Temperature of cooling, − 40° C. Initial elongation, 200%	% permanent set of specimens vulcanized at 143° C. for time				
	10 min.	15 min.	20 min.	25 min.	30 min.
Compound 4	33	16	11	9	9
Compound 5	36	13	11	10	9

ness. To answer this question compound No. 6 was vulcanized in sheets 1, 2 and 4 mm. thick at 138° C. for 25 minutes; the test-pieces were tested for freezing at temperatures of −10° and −40° C. As will be seen from Table XIV and Figure 8, the differences in freezing between samples of different thickness are so small that they need not be taken into consideration; hence, whenever it is necessary to investigate rubber goods of 3 or 4 mm. thickness, samples cut from them can be tested at their normal thickness without first buffing them down. It is seen, therefore, that in this respect rubber behaves in the freezing test otherwise than in tensile tests, where increase of the thickness of the samples leads to lower results.

The question of the behavior of rubber shock-absorbers at low temperatures will now be considered. Airplane and balloon shock-absorbers work at low temperatures during flying, balloon shock-absorbers work at a maximum elongation of 280 to 300%, the airplane ones at a stretch of 20%. The airplane shock-absorbers are stretched only at the moment of landing of the machine, the elongation then amounting, as with the balloons, to 280 to 300%, but it will of

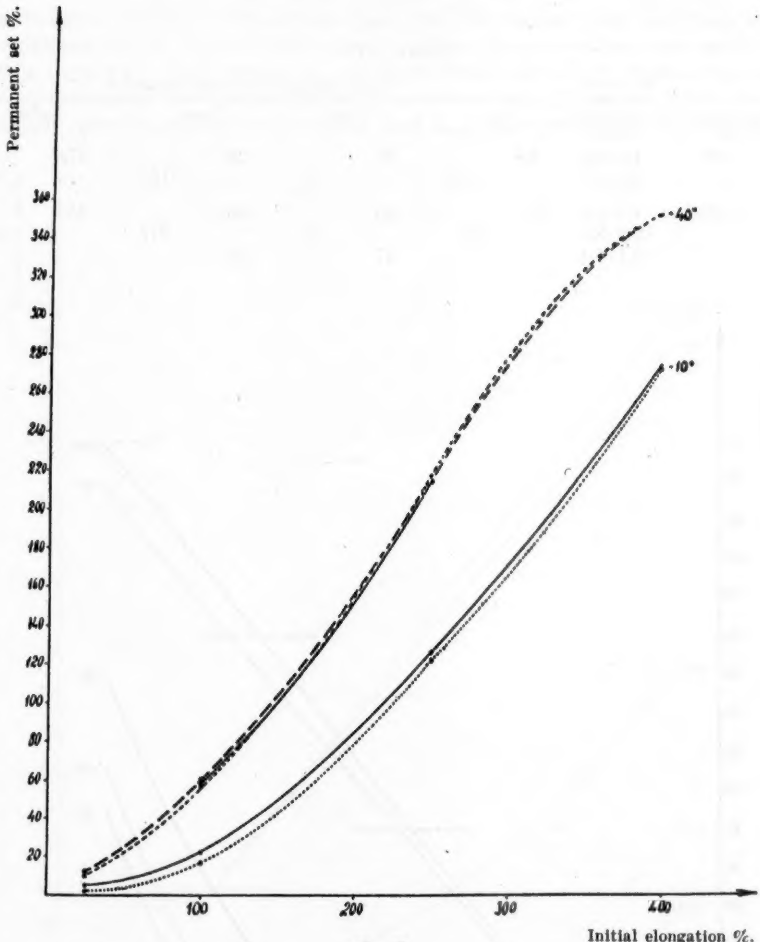

Fig. 8.

COMPOUND No. 4

Smoked sheet	100.0
Sulfur	2.5
Zinc oxide (White Label)	5.0
Stearic acid	2.0
Rezinol F_2	1.0

COMPOUND No. 5

Smoked sheet	100.0
Sulfur	2.5
Zinc oxide (White Label)	5.0
Stearic acid	2.0
Rezinol F_2	1.0
Phenyl-β-naphthylamine	1.0

COMPOUND No. 6

Smoked sheet	100.0
Sulfur	3.0
Zinc oxide (White Label)	20.0
Stearic acid	1.0
Factice	15.0
Paraffin oil	2.0
Whiting	15.0
Clay	30.0
Vulkacit Mercapto	0.8
Antimony sulfide	7.0

TABLE XIV

Temperature of cooling, ° C.	Thickness of tested specimens (mm.)	% permanent set at initial elongation 25%		100%		250%		400%	
—10	1.1–1.3	4.8		22		126		274	
	2.2–2.5		1.6		17		122		272
—40	1.1–1.3	12		60		216		353	
	2.2–2.5		10		56		217		353
	4.1–4.4	—		57		215		—	

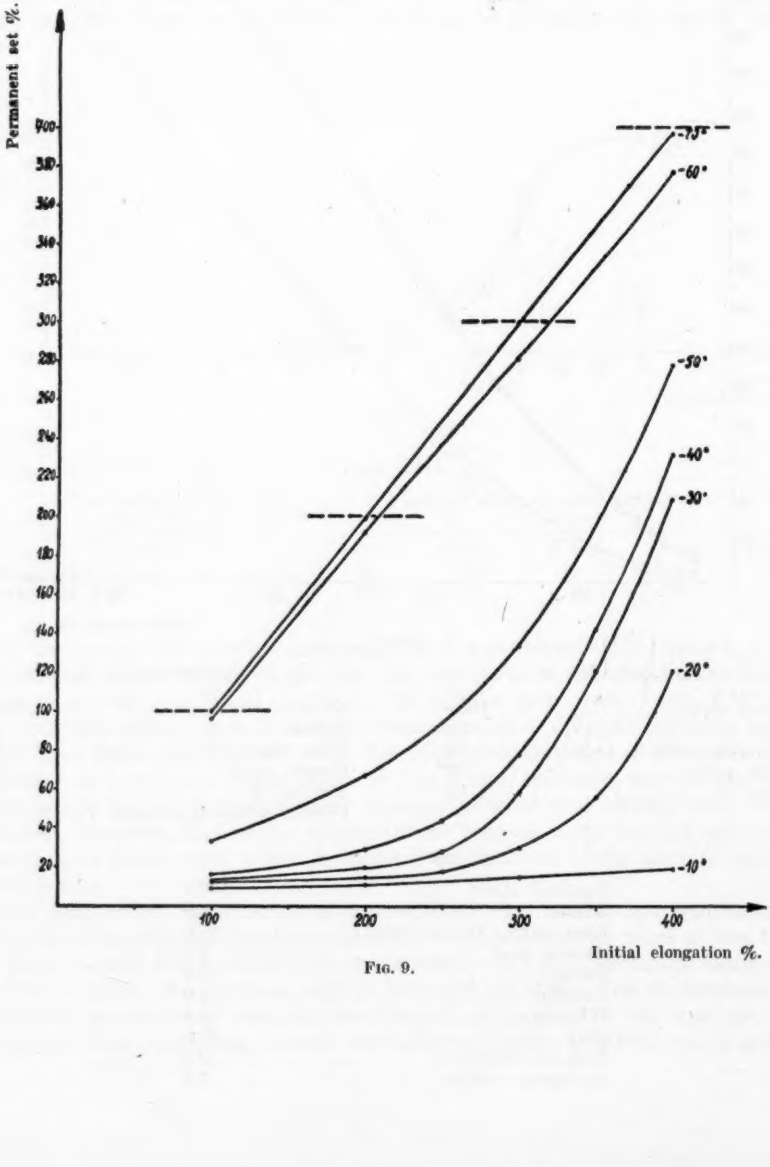

FIG. 9.

course occur at higher temperatures than with balloons as it will take place on the ground and not in the air. Balloon and airplane shock-absorbers are constructed in the same way. They consist of a series of rubber threads of cross-section about 0.9 sq. mm. each, tightly bound by an external braiding. The entire shock-absorber must be resistant to low temperatures, that is, it must not stiffen or crack or lose

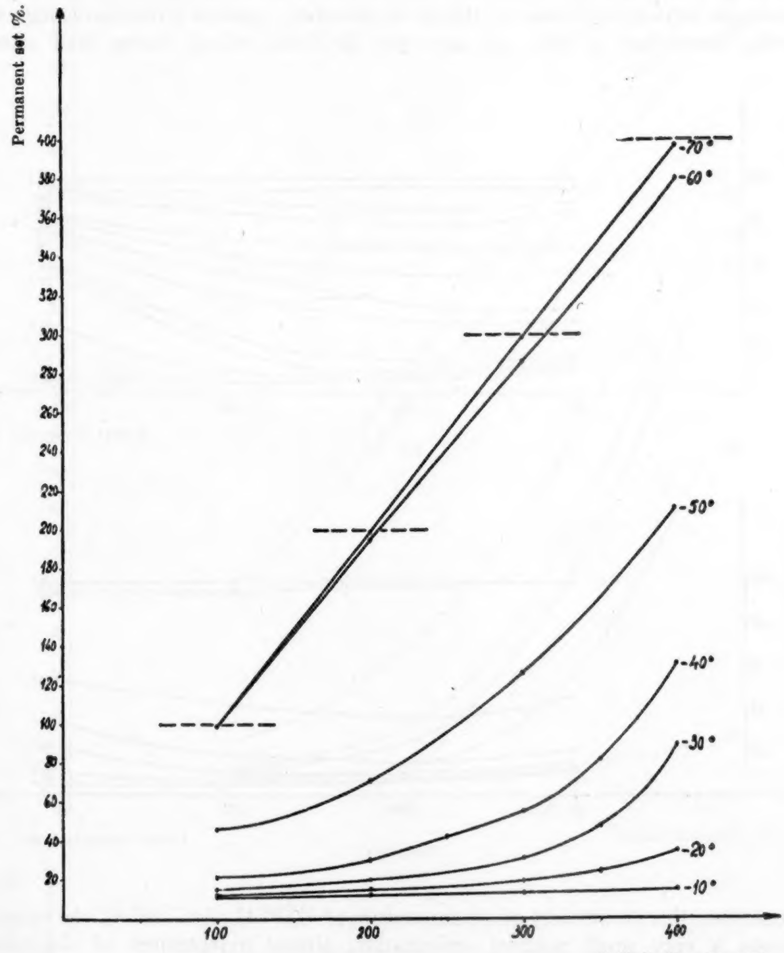

FIG. 10.

its elastic properties in general at such temperatures. As the investigation of the shock absorber as a whole, as well as of its individual rubber threads, was relatively troublesome with our apparatus, we used test-pieces cut out from vulcanized rubber sheets, furnished by a factory where they were prepared for cutting into shock absorber thread. The freezing-resistance of these samples was determined at temperatures from $-10°$ to $-70°$ C. and with initial elongations of 100 to 400%. It is obvious from Table XV and Figures 9 and 10 that the "pure" rubber com-

pound used in the shock-absorbers has a very great freezing-resistance until a temperature of $-40°$ C. is reached. Table XVI and Figures 11 and 12 serve as a better illustration of this effect, the data having been recalculated as percentage of the initial elongation at which the test-pieces were frozen, instead of the half-circumference of the unstretched sample. It will be seen from these figures that the samples, even at a temperature of $-40°$ C. and in initial elongation of 300% (the maximum working extension of the shock absorber), possess a residual elongation hardly amounting to 26% and are very far from entirely losing their elastic

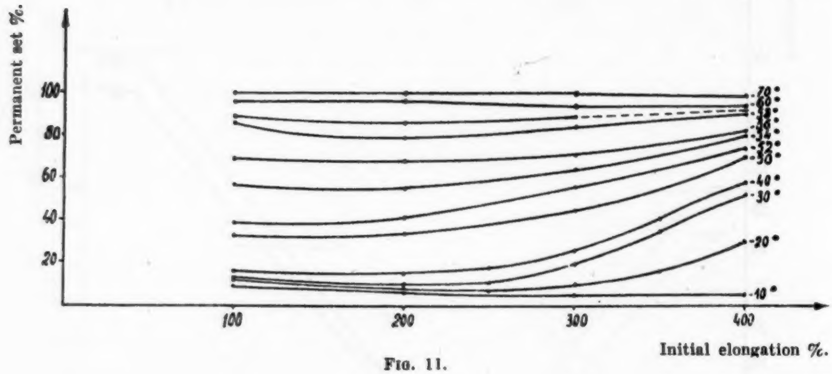

FIG. 11.

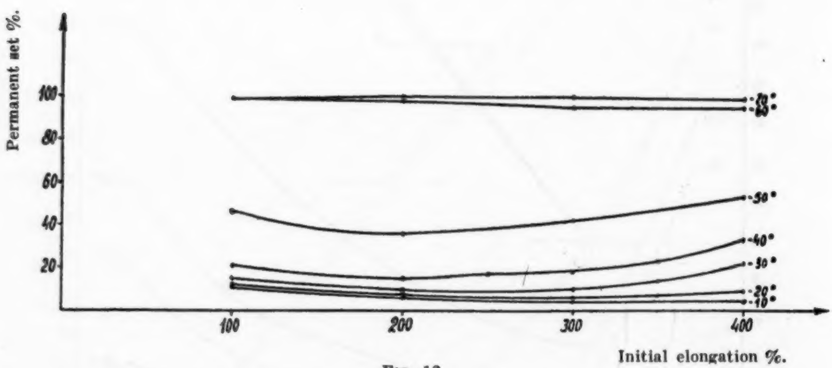

FIG. 12.

properties; this occurs only at a temperature of $-70°$ C. At $-10°$ C. the samples possess a very small residual deformation, almost independent of the initial elongation. With lowering of the temperature down to $-40°$ C. there is a marked increase of freezing for initial elongations of 100 to 200%, while for 300% and higher elongations this increase is greater. A very rapid increase of freezing for smaller as well as greater initial elongations takes place between $-50°$ and $-60°$ C.; it is less pronounced between $-40°$ and $-50°$ C. An entire loss of elastic properties of the samples occurs for lower initial elongations at $-70°$ C., but it is not complete, even then, for higher initial elongations. Apart from "pure" rubber sheet, samples of a loaded compound were investigated also; this, as will be seen from Table XVII, Figure 13, and Table XVIII, Figure 14, gives greater

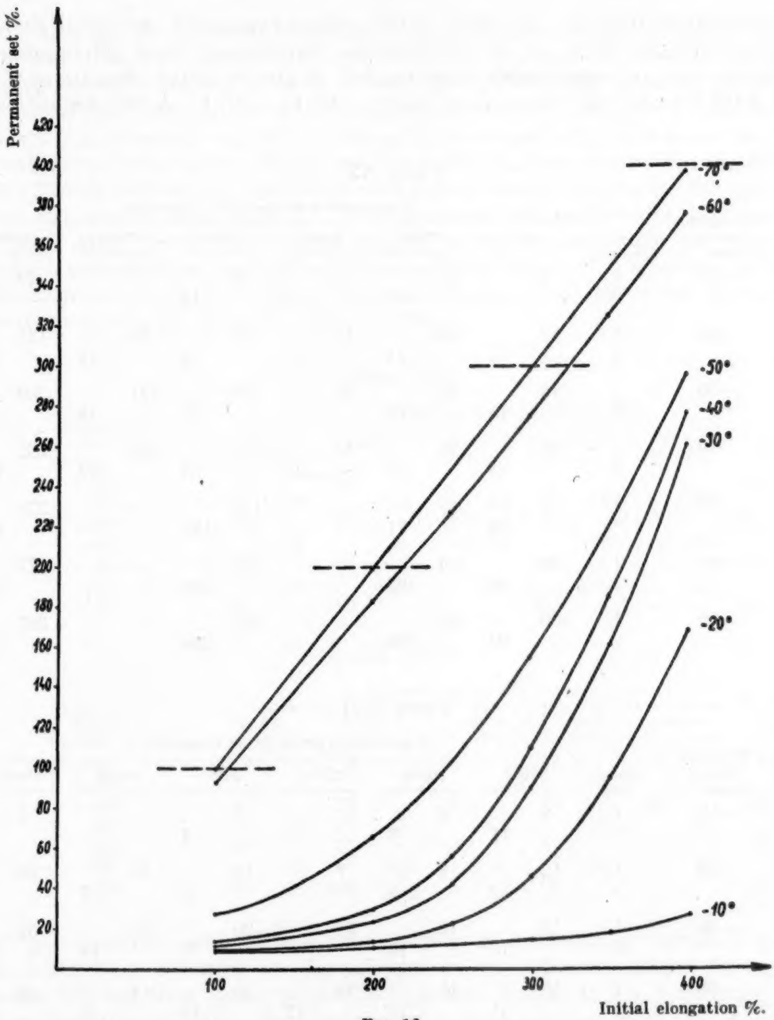
Permanent set %.
Initial elongation %.
-70°
-60°
-50°
-40°
-30°
-20°
-10°

FIG. 13.

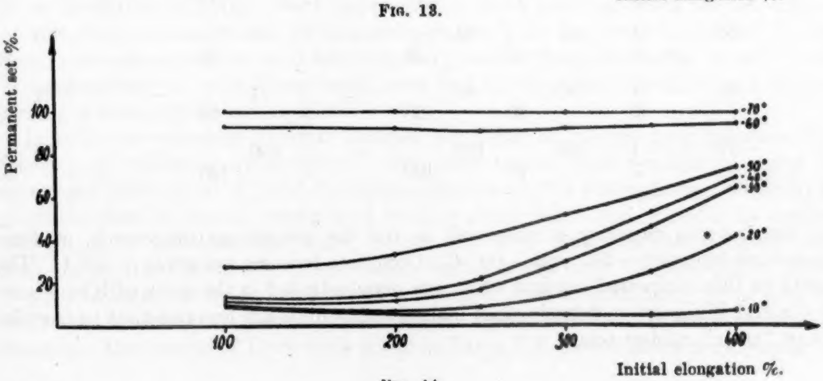
Permanent set %.
Initial elongation %.
-70°
-60°
-50°
-40°
-30°
-20°
-10°

FIG. 14.

freezing values than the preceding "pure" rubber compound. At initial elongations of 100 and 200%, at the temperatures investigated, these differences are negligible, but are considerably more marked at greater initial elongations (300 and 400%) within the temperature limits −20° to −30° C. A very big increase

TABLE XV

Temperature of cooling, ° C.	Specimen.	% permanent set at initial elongation 100%	200%	250%	300%	350%	400%
—10	1	9	11	—	15	—	19
	2	11	12	—	13	—	15
—20	1	12	15	18	30	56	121
	2	12	15	—	19	24	35
—30	1	13	20	28	59	121	209
	2	15	20	—	31	48	89
—40	1	16	29	44	78	142	232
	2	21	30	42	55	82	131
—50	1	33	67	—	134	—	278
	2	46	71	—	126	—	211
—60	1	96	192	—	281	—	377
	2	99	195	—	286	—	380
—70	1	100	199	—	299	—	397
	2	99	199	—	299	—	397

TABLE XVI

Temperature of cooling, ° C.	Specimen	% permanent set at initial elongation 100%	200%	250%	300%	350%	400%
—10	1	9	6	—	5	—	5
	2	11	6	—	4	—	4
—20	1	12	8	7	10	16	30
	2	12	8	—	6	7	9
—30	1	13	10	11	20	35	52
	2	15	10	—	10	14	22
—40	1	16	15	18	26	41	58
	2	21	15	17	18	23	33
—50	1	33	34	—	45	—	70
	2	46	36	—	42	—	53
—60	1	96	96	—	94	—	94
	2	99	98	—	95	—	95
—70	1	100	100	—	100	—	99
	2	99	100	—	100	—	99

in the freezing capacity is observed, as for the preceding compounds, at temperatures between −50° and −60° C. Complete freezing occurs at −70° C. The tests on this compound confirm what was demonstrated in the work of Khvostovskaya and Margaritov, namely, that loaded compounds are less resistant to freezing than "pure" rubber ones.

In addition to the above-described experiments on rubber sheets for shock-absorber thread, we made longer tests on similar samples, the freezing treatment lasting six days; the temperature of test was $-20°$ C. with an initial elongation of 100%. The temperature in the Dewar vessel was kept at $-20°$ C. (maximum $-18.5°$ C., minimum $-21.5°$ C.) during 12 hours each day, at 8 p. m. the temperature was lowered to $-22°$ C. and the vessel was kept covered for the following 12 hours without any addition of solid carbon dioxide. At 8 a. m. the temperature had risen to about $-10°$ C. The experiment was continued in this way for 6 days. After this period the load applied to stretch the sample was taken off and the permanent set was read after one minute's recovery; it amounted to 24%. Therefore, in comparison with a 5-minute freezing period this result is twice as great, since with the latter we obtained 12%.

TABLE XVII

Temperature of cooling, ° C.	% permanent set at initial elongation					
	100%	200%	250%	300%	350%	400%
—10	9	11	—	15	18	27
—20	10	14	23	46	95	168
—30	12	24	42	90	161	261
—40	14	30	56	110	185	277
—50	28	66	—	155	—	296
—60	93	183	227	275	325	376
—70	100	199	—	298	—	397

TABLE XVIII

Temperature of cooling, ° C.	% permanent set at initial elongation					
	100%	200%	250%	300%	350%	400%
—10	9	6	—	5	5	6.8
—20	10	7	9.2	15	27	42
—30	12	12	17	30	46	65
—40	14	15	22	37	53	69
—50	28	33	—	52	—	74
—60	93	92	91	92	93	94
—70	100	100	—	99	—	99

This experiment was made for the purpose of determining whether airplane shock-absorbers mounted on the machine in an unheated hanger during the winter will lose their elastic properties to a high degree. It was ascertained that at an elongation of 100% (the elongation of a shock absorber when the airplane is at rest does not amount to 100%), even during a six-day period at $-20°$ C., no dangerous consequences need be expected; such conditions would be met with in hangers only in quite exceptional cases and in temporary sheds, others always having a temperature above 0° C.

In order to ascertain in what manner the aging of rubber may influence the freezing of rubber shock-absorbers, they were tested after accelerated aging in an oxygen bomb at 60° C. and an oxygen pressure of 21.5 atmospheres. Table XIX gives the data for tensile strength of samples from sheets Nos. 1 and 2, as well as test-pieces of a loaded compound, before and after this accelerated aging test. Test-pieces from sheet No. 2 were aged for 96 hours only. Samples from sheet No. 1 and from the loaded compound were aged until they had lost 30 to 40% of their tensile strength. After the accelerated aging, the samples were tested for freezing. The results of these tests given in Table XX prove that a slight aging of

rubber (8 to 14% loss of tensile product) has no influence on its freezing either at −10° or −60° C. There are, indeed, certain differences in the value of permanent set at initial elongations of 100 to 400%, but they are negligible and lie chiefly within the limits of experimental error. On the contrary, at a temperature of −40° C. with an initial elongation of 400% the values of the permanent set of samples aged for 96 hours are lower than the corresponding values for samples before aging, as will be seen from the results for sheets Nos. 1 and 2. The permanent set of samples subjected to more prolonged aging, which have lost 20 to 40% of their tensile product, did not show greater changes at temperatures of −10° and −60° C. in relation to measurements taken before aging, but at temperatures of −40° and −50° C. there is observed a curious fact, namely, that the permanent set increases with initial elongations of 100 and 200%, remains

TABLE XIX

		Before aging	After 96 hours' aging	After 144 hours' aging	After 192 hours' aging	After 240 hours' aging	After 264 hours' aging	After 312 hours' aging	After 360 hours' aging
Sheet for shock-absorber thread, No. 2.	Tensile strength, kg./cm.²	172	151	—	—	—	—	—	—
	Elongation at break, %	808	790	—	—	—	—	—	—
	Tensile product	139.0	119.3	—	—	—	—	—	—
	Loss of tensile product, %	—	14.2	—	—	—	—	—	—
Sheet for shock-absorber thread, No. 1.	Tensile strength, kg./cm.²	231	230	226	215	—	208	175	174
	Elongation at break, %	808	746	742	739	—	715	750	729
	Tensile product	186.6	171.6	167.7	158.9	—	148.9	131.3	126.8
	Loss of tensile product, %	—	8.0	10.1	14.8	—	20.2	29.6	32.0
Sheet of loaded compound.	Tensile strength, kg./cm.²	227	206	164	150	136	—	—	—
	Elongation at break, %	791	766	729	722	712	—	—	—
	Tensile product	179.6	157.8	119.6	108.3	96.8	—	—	—
	Loss of tensile product, %	—	12.1	33.4	39.7	46.1	—	—	—

almost unchanged with an elongation of 300% and falls considerably with 400%. This behavior of aged samples, as well as the effects taking place in the freezing of rubber at various temperatures, indicates that we have to deal here with effects depending on the internal structure of the rubber molecules. If there were only an increasing immobilization of rubber molecules with lowering of temperature, a curve of homogeneous character would be obtained. The character of the curves, however, changes in passing from a temperature of −10° to −30° C.; these changes become still more obvious within the temperature range −50° to −60° C. It is equally characteristic that the loss of elastic properties at −70° C. is complete only with initial elongations of 100 and 200%, while with initial elongation of 300 and 400% the elastic properties are retained in a very small degree. This means that there occurs an opposite effect to that at higher temperatures, where a greater freezing takes place with greater initial elongations. It has not yet been possible to explain this effect from a theoretical point of view, as we are not specialists in the domain of research on rubber structure. Only one point need be men-

tioned, namely that the researches of Le Blanc and Kröger on the properties of rubber at low temperatures, and the conclusions those authors drew from their work, could not be confirmed in our laboratory. They state that raw rubber acquires at a temperature of $-50°$ C. the character of vulcanized rubber. If, however, as appears from our experiments, it loses at this temperature in a great degree (and at the higher elongations almost entirely) its elastic properties, there can be no question of its complete analogy with vulcanized rubber.

Table XX

	Temperature of cooling, ° C.		% permanent set at initial elongation 100%	200%	300%	400%
Sheet for shock-absorber thread, No. 2.	—10	Before aging	11	12	13	15
		After 96 hours' aging	11	13	15	19
	—40	Before aging	21	30	55	131
		After 96 hours' aging	24	37	61	122
	—50	Before aging	46	71	126	211
		After 96 hours' aging	49	84	133	212
	—60	Before aging	99	195	286	380
		After 96 hours' aging	98	193	286	382
	—70	Before aging	99	199	299	397
		After 96 hours' aging	—	199	—	398
Sheet of loaded compound.	—10	Before aging	9	11	15	27
		After 96 hours' aging	10	12	16	26
		" 144 " "	12	15	18	28
		" 240 " "	12	15	18	24
	—40	Before aging	14	30	110	277
		After 96 hours' aging	17	—	93	—
	—50	Before aging	28	66	155	296
		After 144 hours' aging	45	75	147	267
		" 240 " "	45	78	143	269
	—60	Before aging	93	183	275	376
		After 96 hours' aging	92	183	273	377
		" 144 " "	95	183	280	386
		" 240 " "	—	184	—	370
Sheet for shock-absorber thread, No. 1.	—10	Before aging	9	11	15	19
		After 96 hours' aging	9	11	13	15
		" 264 " "	11	—	15	17
		" 312 " "	14	—	19	19
	—40	Before aging	16	29	78	232
		After 96 hours' aging	15	—	64	207
		" 264 " "	21	—	66	159
		" 312 " "	26	37	70	172
	—50	Before aging	33	67	134	278
		After 264 hours' aging	43	77	134	246
		" 312 " "	48	82	133	239
	—60	Before aging	96	192	281	377
		After 96 hours' aging	95	186	273	369
		" 264 " "	96	190	280	375
		" 312 " "	97	189	278	379

CONCLUSIONS

(1) Raw rubber, smoked sheet as well as crepe, freezes to a high degree at low temperatures. The difference between the freezing at $-10°$ and $-60°$ C. is comparatively small at initial elongations of 300 and 400%. With smaller initial elongations there is a greater difference in degree of freezing at temperatures of $-10°$ and $-60°$ C. A complete loss of the elastic properties of the rubber takes place at $-70°$ C.

(2) Previous heating of raw rubber, even at a temperature of 140° C., has no effect on its freezing-resistance.

(3) The susceptibility of rubber to freezing increases with increase of the elongation, this effect being strongly marked above an elongation of 200%.

(4) An increase in the vulcanization temperature, and therefore a shortening of the vulcanizing time, has only an insignificant effect on the freezing-resistance of rubber compounds.

(5) The freezing effect increases as the temperature is lowered.

(6) An entire loss of the elastic properties of vulcanized rubber takes place for the lower initial elongations at a temperature of −70° C.; for higher elongations; however, they are still retanied at this temperature in a very small degree.

(7) "Pure" rubber compounds have a much greater resistance to freezing than loaded ones.

(8) The minimum susceptibility to freezing for loaded compounds is obtained with those that are slightly overvulcanized. At the higher elongations this minimum is distinctly shifted into the region of overvulcanization.

(9) Softeners have in general no effect in reducing susceptibility to freezing.

(10) The use of phenyl-β-naphthylamine has no effect on the susceptibility to freezing.

(11) The aging of rubber, even when producing 40% of loss of tensile product, has no effect in lowering its resistance to freezing either at −10° or −60° C. and at initial elongations of from 100 to 400%. On the other hand, the resistance to freezing of aged samples is less at temperatures of −40° and −50° C. with initial elongations of 100 to 200%; at an initial elongation of 300% they show almost no change in relation to unaged samples, while at an elongation of 400% they show a distinct increase in resistance to freezing.

(12) Airplane and balloon shock-absorbers of "pure" rubber compounds possess, within the limits of their elongation during use, even at a temperature of −40° C., quite insignificant susceptibility to freezing. An entire loss of their elastic properties occurs at −70° C.

(13) Keeping airplanes in improvised sheds in winter time even at −20° C. has practically no effect on the usefulness of rubber shock-absorbers.

It is obvious that this applies only to properly vulcanized shock-absorber rubber. The determination of the influence of the degree of undervulcanization of rubber threads on their freezing-resistance will be the subject of further work.

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THE TESTING OF RUBBER AT LOW TEMPERATURES *

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INTRODUCTION

Developments in modern compounding have in the last few years undoubtedly improved the general properties of vulcanized rubber. Ever-widening fields of application of rubber goods have extended the range of temperature over which rubber is expected to retain its properties. The search for rubber compounds that shall have greater resistance to oxidation, heat, oil and so forth has certainly been pushed forward with great success, but progress in the other direction, namely, towards rubber compounds resistant to extreme cold, does not appear to have been so rapid.

In this country we do not experience the extreme cold which occurs in the upper atmosphere and in regions nearer the poles, but rubber suspension systems, etc., as used in ships in polar latitudes or vessels transporting foodstuffs, railway components of many kinds and the numerous rubber parts used in the construction of aircraft all suffer to some extent from loss of resilience when exposed to cold conditions. It therefore seems just as necessary to compound with a view to resisting changes induced by freezing as we normally do to resist heat. With this end in view it was decided to make a critical review of published data on the effect of low temperatures on rubber to serve as a guide to further practical work.

As is to be expected, those countries experiencing great cold have already carried out considerable investigation, but the available information is fairly widely distributed, and no doubt there is much work of a private nature which has never been published. It will be convenient, in the summary which follows, to indicate the most important information under headings relating to the chief properties of rubber. As is so frequently the case, physical results have been obtained on mixings of unstated composition or state of vulcanization, or on mixings that are simple, no doubt, from the theoretical standpoint but almost unusual from the practical point of view.

EFFECT OF COLD ON TENSILE PROPERTIES

In 1910 Breuil[1] described the behavior of three rubber compounds, "pure gum," a litharge-accelerated mix and a "technical" mix of that day, between temperatures of −10° C. and +100° C. Polanyi and Schob[2], on an unspecified rubber at −190° C., and Mark and Valkó[3], on accelerated "pure gum" and gas black stocks at −195° C., conducted their experiments to much lower temperatures, and the latter investigators found that not only was the tensile strength increased several-fold at that temperature, but that by stretching the samples before freezing the frozen gas black stock showed a tensile strength as high as 3720 kg. per sq. cm. (18 tons per sq. in.), based on the cross-section after extension. Le Blanc and Kröger[4], examining a "pure gum" stock from −54° C. upwards, found marked hardening particularly of the undervulcanized samples.

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The most extensive work, however, was published by Tener, Kingsbury and Holt[5]. They used six compounds ranging from "pure gum," unaccelerated, to loaded reclaim mixes, vulcanized to optima, judged by maximum tensile strength at normal temperatures. Ring test-pieces cooled to the temperature of test for 5 minutes in air or 2 minutes in alcohol were used, and the main conclusions reached were: that all the compounds were rigid below −60° C. (at −75° C. the samples could be broken with a sharp blow); stiffening with decreasing temperature was very marked; changes of temperature had less effect on uncompounded rubbers than on loaded compounds; several cycles of freezing and thawing did not affect the rubbers; finally differences due to the compounding ingredients present were solely in degree and not in kind. This is important since it makes the search for cold-resistant rubber the more difficult. Somerville and Cope[6] recorded the effect of the sulfur content, composition of the mix and its previous history. Somerville and Russell[7] examined the tensile properties of vulcanized rubber as represented by commercial inner tubes and found little correlation between tensile strength, modulus and permanent set when testing at 0° C., 25° C. and 100° C.

EFFECT OF COLD ON PERMANENT SET

Practically no work has been recorded on the effect of freezing on the permanent set of rubber. Wormeley[8] reported results on an unspecified compound and worked only from 48° F. (9° C.) upwards. The indications were decreasing set with increasing temperature, and that the set did not vary directly in proportion to the elongation effected. Somerville and Russell[7] stretched their tubes to 400%, held them for 16 hours at room temperature, immersed them for 1 hour in ice-water, after which the samples were cut and measured in the ice water after a lapse of 5 minutes. The conclusion was reached that high set probably indicated low sulfur ratios. Work in the author's laboratory on compounds of known composition, as reported later, confirms this opinion. The complete retention of elongation when the rubber is frozen to −70° C. is the basis of the T-50 test which is described later.

EFFECT OF COLD ON HARDINESS AND ELASTICITY

Most of the recorded work on this subject appears in Russian or Japanese, and the available abstracts give the general conclusions without the experimental data on which they are based. Khvostovskaya and Margaritov[9] state that total loss of elasticity occurs below −55° C. (cf. *supra,* Tener, Kingsbury and Holt[5], and also Somerville[10]). They recommend short high-temperature vulcanization, and state that filler contents should be low. Fujiwara and Tanaka[11] recommend low-sulfur short vulcanization (to avoid depolymerization presumably), and state that at a given low temperature the more highly vulcanized the rubber the harder it becomes. This observation appears to conflict with other evidence, as will be shown later. Nagai[12] describes a useful apparatus for the estimation of hardness at low temperatures, but is compelled to use a penetrometer which differs from those common to the rubber trade. He states that hardness increases hyperbolically with decrease of temperature, and points out that those softeners in common use in the rubber industry, which solidify above −50° C., are no use in compounding rubber to resist cold. Unfortunately those low-viscosity softeners which do not freeze above −50° C. so reduce the tensile strength of the rubber as to make it valueless.

EFFECT OF COLD ON HYSTERESIS AND FATIGUE

Asahina, Hachiya and Ogawa[13] quote hysteresis value from 0° to −60° C., while Khvostovskaya and Margaritov[14] describe the effect of low temperature on hysteresis, and indicate that low filler loadings are desirable, since the internal friction is increased at low temperatures. Douglas[15] examined the dynamic compression at low temperatures of rubber suitable for aircraft tail-skid rings, and concluded that the results did not agree with the behavior of rubber in cold climates. Somerville[16] found that both gas black and "pure gum" stocks had a longer fatigue life at −10° C. than at +20° C., and attributed this to the higher permanent set of the two stocks at the lower temperature. Similarly he found a longer flexing life at 0° C. than at +20° C.

EFFECT OF COLD ON ELECTRICAL PROPERTIES

An extensive examination of the volume resistivity, permittivity and power factor of deproteinized rubber vulcanized solely with sulfur has been made from −75° C. upwards by Scott, McPherson, and Curtis[17]; apart from this work there appear to be no other published records.

EFFECT OF COLD ON THERMAL BEHAVIOR

Stifler and Mitchell[18] examined the elastic constants and thermal expansion of rubber at −30° C.

EFFECT OF COLD ON PERMEABILITY

Little published work appears on this subject, which is obviously one of considerable importance. Barr and Thomas[19] found that the permeability of rubber-covered cotton to hydrogen was lower, after keeping the sample for 5 hours at −15° C. and then crumpling, than it was in the unaged, untreated condition.

EFFECT OF AGING IN THE COLD

Included among the series of aging conditions to which eight different high zinc oxide stocks were subjected[20] is storage for 107 weeks at −11° C. After this aging period the standard determinations of tensile strength and elongation, permanent set, energy return, hardness and swelling were carried out. The results indicate that rubber is not unduly harmed by such storage conditions.

THE T-50 TEST

As was observed under the heading of permanent set, rubber stretched and cooled below −65° to −70° C. retains its extension and does not retract until warmed again to higher temperatures. The behavior of rubber so treated was examined by Gibbons, Gerke and Tingey[21], who developed the T-50 test, in which the temperature is determined at which a sample of rubber previously stretched and frozen retracts to half the original elongation. The method is excellently described and a new weapon added to the armory of the rubber technologist. The T-50 test is a rapid means of determining the state of vulcanization of a given vulcanizate, but it does not predict in any way the other physical requirements of aging, flexing, abrasion resistance, etc. The T-50 temperature is roughly proportional to combined sulfur in any one mix, and gives a measure of the state of vulcanization independent of the physical properties which depend

on its composition. The method is also described in a trade publication[22], while Haslam[23] records a new method of interpreting the results obtained, using zinc oxide mixings. Tuley[24] gives further particulars of the application of the test in relation to variations in compounding, *i.e.*, the effect on the state of vulcanization arising from the use of antioxidants, anti-scorching materials and low sulfur compounding.

EXPERIMENTAL

As has already been indicated, the effect of cold on the permanent set of rubber vulcanizates has been imperfectly investigated. It was therefore decided to examine three stocks of similar loading, but containing varying sulfur ratios. In order to avoid as many variables as possible, high zinc oxide stocks capable of industrial use were selected, having the following compositions (all parts by weight):

	Stock A	Stock B	Stock C
1st Latex crepe	100	100	100
Fine-particle French process zinc oxide	135	135	135
Stearic acid (tech., m.p. 130° F.)	1	1	1
Paraffin wax (tech., m.p. 120° F.)	2	2	2
Phenyl-β-naphthylamine (AgeRite Powder)	1	1	1
Sulfur (ground)	2.75	0.5	—
Tellurium (Telloy)	—	0.5	0.5
Tetramethylthiuram disulfide (Tuads)	0.1	0.5	3.0
Benzothiazyl disulfide (Altax)	1.0	1.0	—
Mercaptobenzothiazole (Captax)	—	—	0.5

Each stock was milled under as far as possible identical conditions; the usual resting period of 24 hours was allowed before vulcanizing in sheets 0.1 inch thick at 20 lbs. per sq. in. steam pressure.

Tensile determinations were carried out on standard dumb-bell samples, press-punched along the grain, using a Scott machine.

Hardness figures were obtained with a standard Shore durometer, samples being piled one upon another in sequence of vulcanizing times. Hardness tests were done before and after freezing. For simplicity one freezing temperature, *viz.*,—10°C., was selected, and this was obtained in a modified domestic refrigerator. Samples were supported on wire grids in air kept as dry as possible to avoid frosting of the freezing unit.

Permanent set determinations were carried out on strips 0.5 inch wide. These were stretched on a rack by 200% of the original length between accurate bench-marks, held in that position 18 hours, released and measured after a lapse of 6 hours.

TENSILE

Vulcanization at 20 lbs.	Stock A (1)	Stock A (2)	Stock A (3)	Stock B (1)	Stock B (2)	Stock B (3)	Stock C (1)	Stock C (2)	Stock C (3)
10 minutes	Unvulcanized			Unvulcanized			350	460	575
15 "	"			1275	1430	540	600	1100	625
20 "	1925	3650	675	1860	3550	675	840	2000	720
30 "	2200	3660	650	1950	3600	660	1260	2825	700
45 "	2000	3450	630	2000	3550	650	1600	3000	630
60 "	1780	3060	620	1950	3425	630	1750	3000	625

(1) Lbs. per sq. in. at 500% extension.
(2) Lbs. per sq. in. at break.
(3) Elongation (%) at break.

HARDNESS (Shore)

	Stock A		Stock B		Stock C	
	18° C.	−10° C.	18° C.	−10° C.	18° C.	−10° C.
10 minutes	—	—	—	—	30	45
15 "	—	—	35	49	38	47
20 "	48	52	45	50	40	48
30 "	54	55	47	51	42	50
45 "	53	55	47	51	44	50
60 "	52	55	46	52	45	51

PERMANENT SET (%)

	Stock A		Stock B		Stock C	
	18° C.	−10° C.	18° C.	−10° C.	18° C.	−10° C.
10 minutes	—	—	—	—	20	120
15 "	—	—	9	70	15	50
20 "	7	17	8	40	10	30
30 "	7	10	6	15	8	20
45 "	5	7	5	15	6	15
60 "	5	7	5	15	6	10

The increasing spread between hardness (18° C.) and hardness (−10° C.) as the sulfur ratio is decreased is very apparent, and over the ranges of vulcanization and temperature examined the results lead to conclusions which conflict with those of Khvostovskaya and Margaritov[9] and Fujiwara and Tanaka[11]. The minimum effect of cold on permanent set under the same conditions appears to be obtained with the well vulcanized medium-sulfur mix.

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SOME PROPERTIES OF TWO VULCANIZED PURE GUM COMPOUNDS AT LOW TEMPERATURES *

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INTRODUCTION

Some excellent work has been published by various authors on the effect of low temperatures on the properties of rubber, but the field is still relatively new so that it seems worth while to continue the study along the lines of modern compounding.

Accordingly this laboratory laid out an elaborate compounding and testing program in an attempt to cover the effect at low temperatures on vulcanized rubber of the various classes of compounding ingredients, such as accelerators, antioxidants, fillers, softeners, raw rubbers and reclaimed rubber. The data given in this paper cover only a very small proportion of the total work contemplated, and are confined to the properties of two pure gum compounds. They do not include any specific recommendations for the compounding of rubber to resist the action of very low temperatures.

Ten years ago at the Swampscott, Mass., Meeting of the American Chemical Society we showed that overvulcanized rubber breaks off short when stretched at 100° C. The compounds used at that time were vulcanized with what has come to be known as a normal proportion of sulfur, and no recommendations were made as to how the shortness or brittleness might be prevented. Later, in various issues of the *Vanderbilt News,* it was shown that by the use of what has come to be known as "low sulfur" plus suitable acceleration, the overvulcanized condition above referred to could be prevented, and likewise the resulting shortness or brittleness at 100° C. In most of that past work, physical properties at three temperatures were shown, *viz.*, at 100°, 25° and 0° C. In the present work, physical properties are shown also at −30°, −40°, −50° and −60° C.

TERRESTRIAL COLD SPOTS

Some idea of the low temperatures to which rubber goods may be exposed in service can be gained from Table I, which lists a number of low temperatures recorded at various places in northern latitudes. These data were obtained through the United States Weather Bureau.

APPARATUS FOR PHYSICAL TESTING AT LOW TEMPERATURES

In making physical tests at very low temperatures it was found convenient to break the specimens in acetone kept cold by means of dry ice. Fig. 1 shows a photograph of the special Scott tester, equipped with testing tank and external cooling apparatus used to reach temperatures down to and including −60° C. The cooling system consisted of a cork-lined tank (about 20 inch cube) with close-fitting lid. Within the tank 200 ft. of ⅜-in. copper tubing were coiled, and

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 15, pages 773-785.

this coil was connected through a centrifugal pump to the testing tank in which the specimens were stretched. The testing tank and coil were filled with circulating acetone, which was kept cold by means of dry ice surrounding the coil.

MEASUREMENT OF HARDNESS AT LOW TEMPERATURES

To obtain hardness measurements the samples were laid on a metal plate supported by means of wooden strips directly over a quantity of dry ice contained in a rectangular box. The temperature directly over the metal surface was maintained at the desired level by means of a current of air blown in through the bottom of the box. Hardness readings were taken by quickly raising the lid and placing the Shore instrument on the samples without their removal.

TABLE I

United States	° C.	Canada	° C.	Europe and Asia	° C.
Denver, Col.	—34	Medicine Hat	—33	Sweden (Interior)	—45
Omaha, Neb.	—35	Banff	—34	Finland "	—45
Dubuque Iowa	—35	Edmonton	—36	N. E. Russia	—50
Concord, N. H.	—37	Winnipeg	—38	Lugan, U. S. S. R.	—41
Klukwan, Alaska	—38	Norway House	—46	Orenburg, "	—41
Anchorage, "	—38	Fort Vermillion	—48	Pamirski Post, "	—47
Pierre, S. D.	—40	Prince Albert	—57	Archangel, "	—47
St. Paul, Minn.	—41			Bogoslovsk, "	—49
Helena, Mont.	—41			Ishim, "	—54
Kenai, Alaska	—43			Barnaul, "	—55
Bismarck, N. D.	—43			Yeniseisk, "	—59
Fairbanks, Alaska	—54				
Fort Yukon, "	—57				
Tanana, "	—60				

PREPARATION OF TEST-PIECES

All test-pieces used were dumb-bell test-pieces, $\frac{1}{8}$ inch wide and 1 inch long at the constricted portion, cut from slabs 0.075 inch thick. All slabs were vulcanized in a press at 40 lbs. per sq. in. steam pressure (142° C.). The hardness measurements were made on slabs of the same thickness.

TABLE II

PURE GUM FORMULAS

	A	B
Smoked sheet	100	100
Stearic acid	1	1
Agerite Resin D	—	2
Zinc oxide	10	10
Sulfur	10	2.5
Mercaptobenzothiazole	0.2	1.5

Compound A contains very high sulfur plus a small amount of accelerator to enable it to be vulcanized alongside compound B, which contains a normal amount of sulfur and accelerator. This range of sulfur was chosen to show the possible effect of abnormally high combined sulfur.

Fig. 2 shows the tensile-time of vulcanization curves of compound A at five temperatures. As was to be expected, this compound is slow-vulcanizing, and the tensile strength drops off rapidly beyond the optimum. The curves at four of

the five temperatures are similar in shape, but at 100° C. the falling off in tensile strength beyond the optimum is extremely rapid, as is customary with overvulcanized pure gum stocks tested at this temperature. Note that the

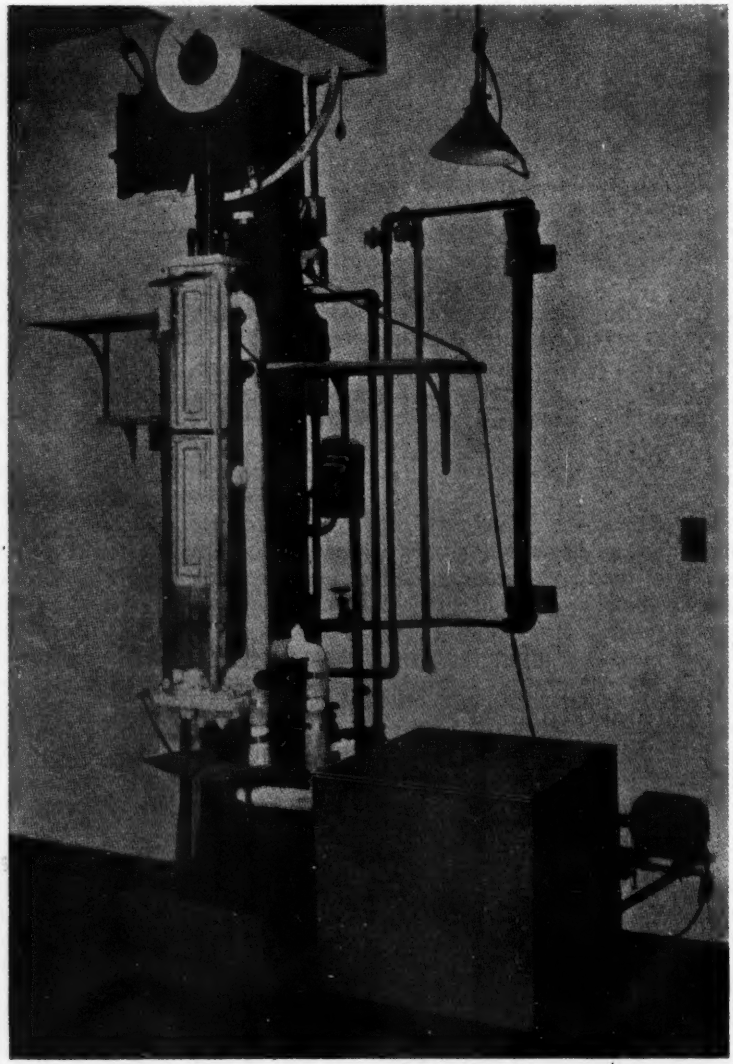

FIG. 1.—Scott tester with tank and cooling equipment.

strength at −60° C. is nearly double the strength determined at room temperature.

The percentage combined sulfur[1] on the rubber content of the compound is also plotted against time of vulcanization, and at the final period of 300 minutes over

80% of the original sulfur is combined. Note that, regardless of the increasing combined sulfur, the spread between the 25° and the −60° curves is practically the same at all vulcanizations.

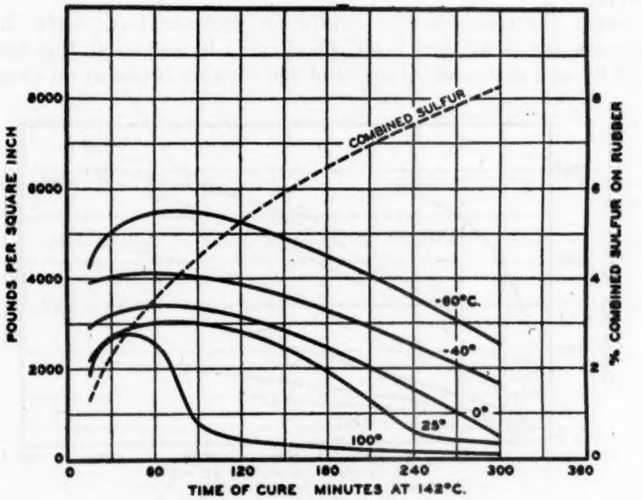

FIG. 2.—Tensile strength. Compound A.

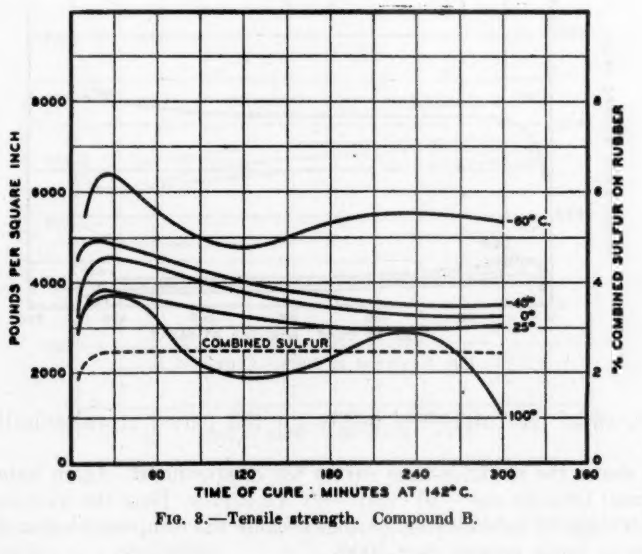

FIG. 3.—Tensile strength. Compound B.

Fig. 3 shows the tensile-time of vulcanization curves for compound B at the same five temperatures. This compound naturally vulcanizes faster than compound A, and the falling off in tensile strength beyond the optimum is much less, even at 100° C. Note that the strengths at all temperatures are higher than with

compound A and that the increase in strength at −60° C., over room temperature, is about the same as with compound A.

The combined sulfur reaches a maximum at the 20-minute vulcanization, and again no correlation exists between combined sulfur and the spread between the various curves.

Fig. 4 shows the modulus-time curves for compound A. Note the extreme spread between the −40° and −60° C. curves. Inasmuch as this modulus was taken at 500% and inasmuch as many of the samples broke at an elongation less

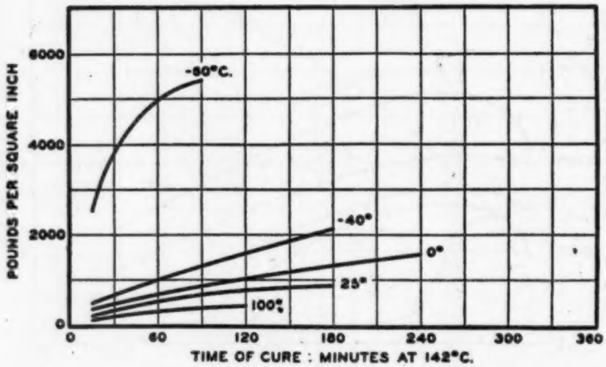

FIG. 4.—Stress at 500%. Compound A.

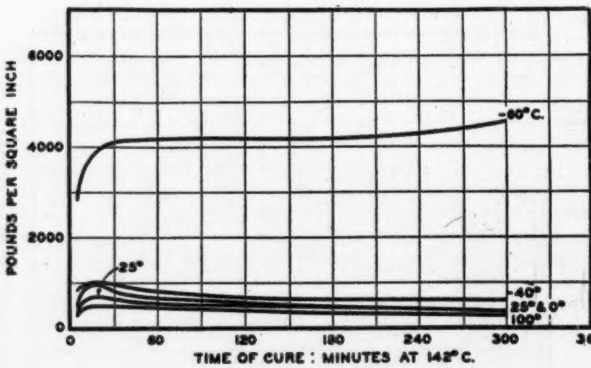

FIG. 5.—Stress at 500%. Compound B.

than this, all of the curves end before the full period of vulcanization of 300 minutes.

Fig. 5 shows the modulus-time curves for compound B. Again note the enormous spread between the −40° and −60° C. curves. Here the modulus is shown for the full range of vulcanization periods because the compound has at all times an elongation at break greater than 500%.

Figs. 6 and 7 show the elongation-time curves of compounds A and B. The outstanding feature of compound A is the extremely sharp decline of the 100° C. curve. In contrast with A, the elongation curves of compound B are characterized by their flatness.

The T-50 value of a rubber compound, as defined by the originators of the test[2], is the temperature in degrees centigrade at which a sample of rubber, stretched by a predetermined amount and frozen, will, when released, retract to 50% of its

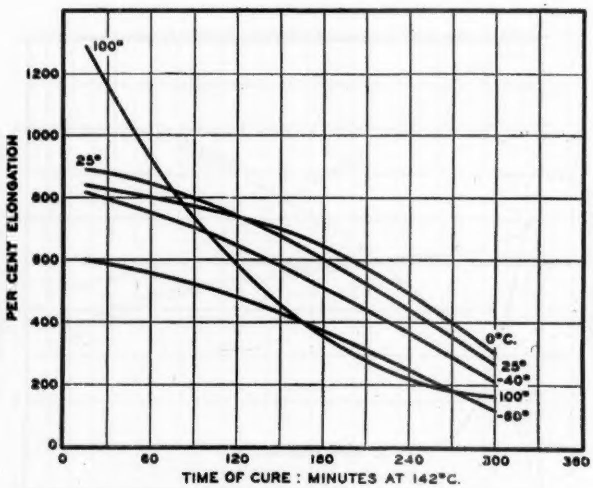

FIG. 6.—Elongation at break. Compound A.

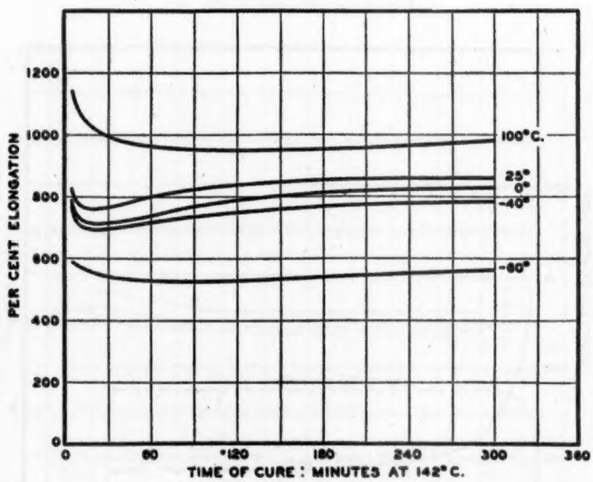

FIG. 7.—Elongation at break. Compound B.

stretched frozen elongation. The T-50 test is a method for determining the state of vulcanization of a compound.

In the case of compound A (Fig. 8) the T-50 values beyond the 90-minute vulcanization were unobtainable because the test strips broke before reaching the elongation of 500% required for a true T-50 value. The T-50 values for compound B (Fig. 9) continue to decrease after the optimum vulcanization, as

judged from tensile strength values, has been passed, while the combined sulfur reaches a maximum at approximately the optimum.

Figs. 10 and 11 show the Shore hardness *versus* time of vulcanization for compounds A and B at different temperatures. At the optimum both compounds have

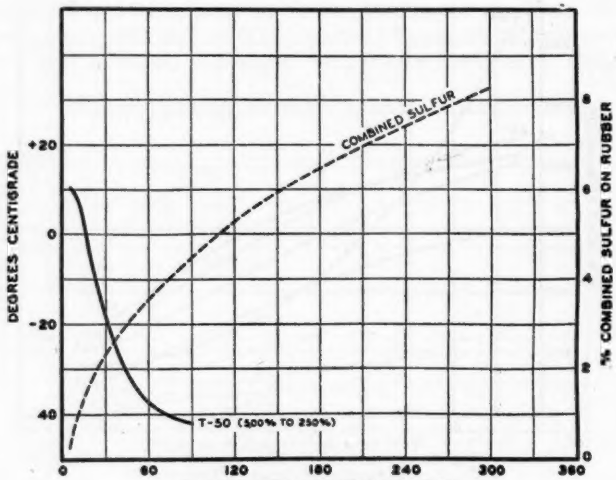

FIG. 8.—T-50. Compound A.

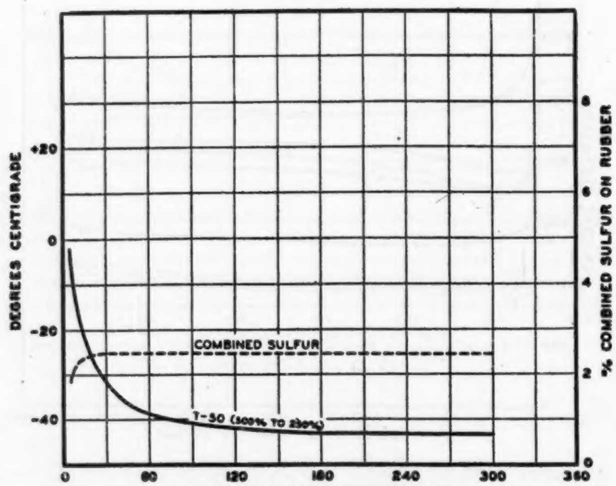

FIG. 9.—T-50. Compound B.

approximately the same hardness. As would be expected the hardness of A increases with vulcanization beyond the optimum, whereas that of B undergoes relatively little change. The outstanding feature of the two compounds is the extremely sharp rise of the −30° C. curve of compound A. Here, therefore,

is an indication that high combined sulfur is not the answer to the problem of resistance to low temperatures.

Figs. 12 and 13 show the effect of time of exposure to cold on the hardness of compounds A and B. In this test only one period of vulcanization of each com-

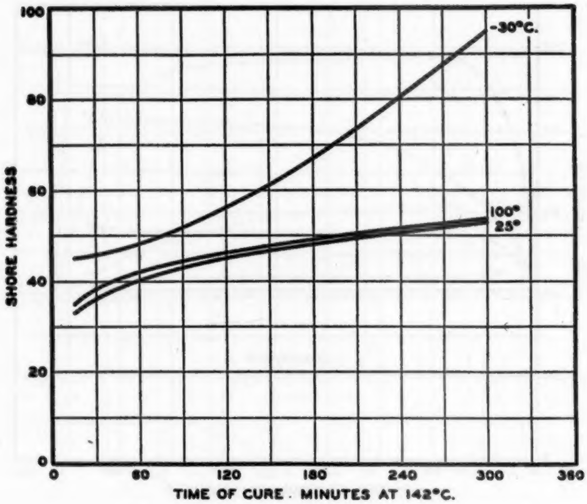

FIG. 10.—Shore hardness. Compound A.

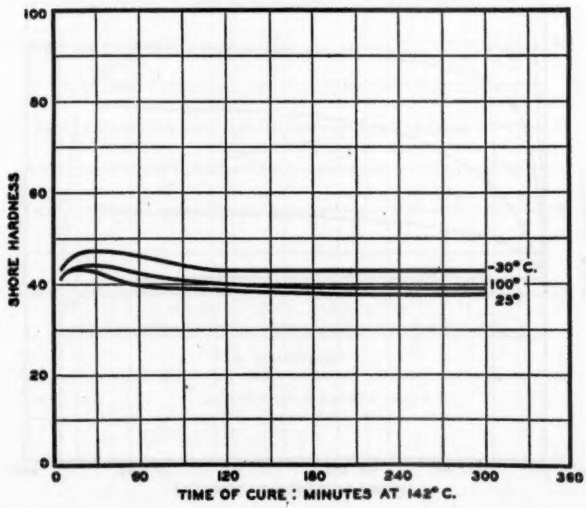

FIG. 11.—Shore hardness. Compound B.

pound was investigated, namely, the optimum (60 minutes for compound A and 20 minutes for compound B). The slabs were placed in the cold box previously described, and their hardness was measured with a Shore durometer at intervals up to 4 hours.

Both compounds harden to the Shore value of 100 at $-60°$ C., which means that they are board-like and brittle. At $-50°$ C. they become practically as hard, though somewhat more slowly. No outstanding differences between the two compounds are apparent, regardless of the fact that there is about 1% difference in

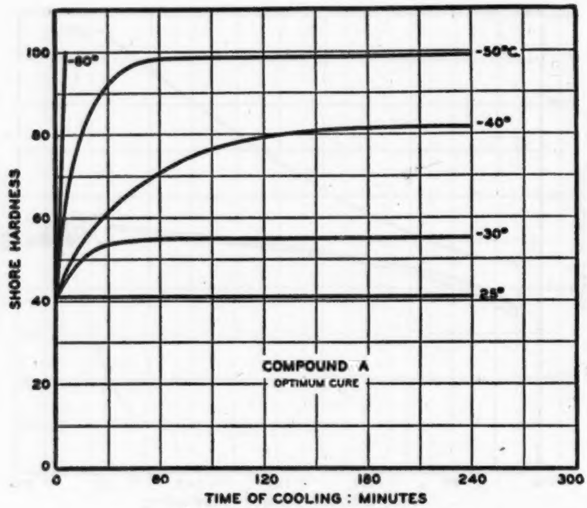

FIG. 12.—Shore hardness *vs.* time of cooling.

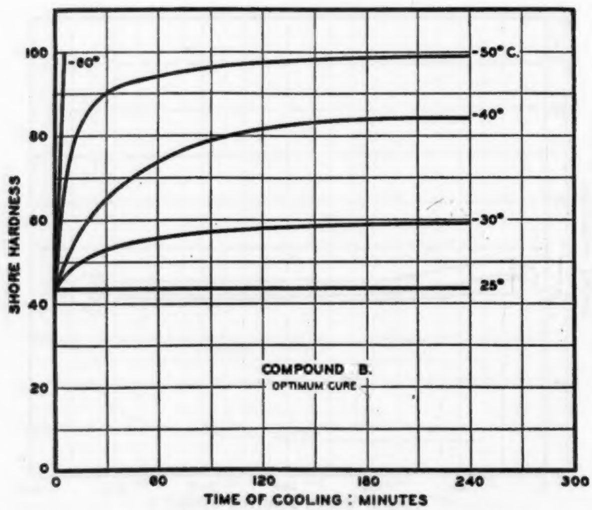

FIG. 13.—Shore hardness *vs.* time of cooling.

combined sulfur between the two samples. The board-like condition at $-60°$ C. is accompanied by such brittleness that the samples can be shattered to pieces with a light hammer blow. This fact in itself was rather to be expected, but it is certainly remarkable that this brittleness should be accompanied by an extensibility

of over 500% for both compounds when tested at $-60°$ C. (Compare Figs. 6 and 7.)

Fig. 14 shows the results obtained after substituting deproteinized rubber for smoked sheet in compound B. Again only one period of vulcanization was used,

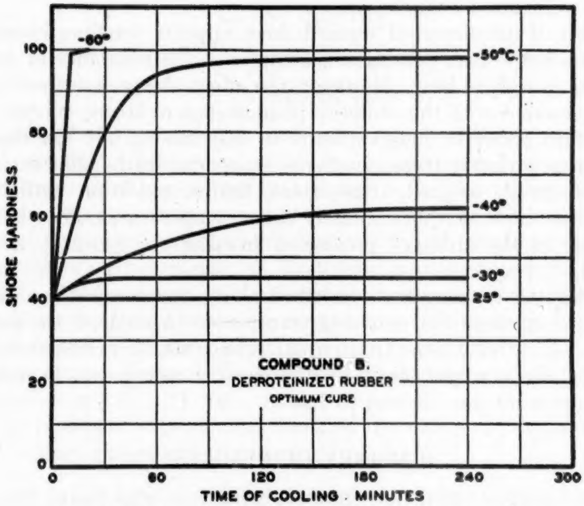

FIG. 14.—Shore hardness *vs.* time of cooling.

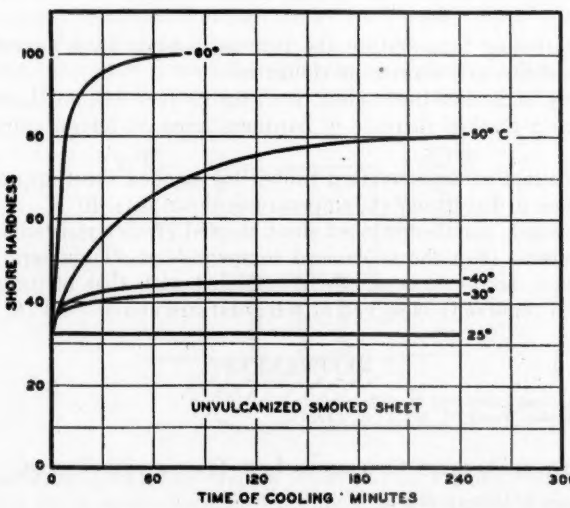

FIG. 15.—Shore hardness *vs.* time of cooling.

namely, the optimum. The hardening at $-30°$ and $-40°$ C. was much less with this compound than with compound B, but at $-50°$ and $-60°$ C. there was no essential difference between the two rubbers.

Fig. 15 represents raw smoked sheet, unmilled but pressed at about 105° C. for

30 minutes in a mould to give a sheet smooth enough for hardness measurements. This raw smoked sheet is softer at room temperature than either of the two pure gum stocks, but the remarkable thing is its resistance to hardening when rapidly cooled to $-40°$ C. At $-50°$ C. it is still softer than the two pure gum compounds. At $-60°$ C. it does become board-like and brittle, but this change is much slower than with the vulcanized compounds.

This behavior of unvulcanized smoked sheet appears startling inasmuch as all rubber chemists know that vulcanization improves the resistance of rubber compounds to cold as well as heat. However, the effect above described is not to be confused or compared with the ordinary phenomenon of frozen rubber, which is a condition brought about by long exposure to only moderately low temperatures. What is known as ordinary frozen rubber is an opaque leather-like material which does not return to its original, transparent, flexible condition until it has been warmed for some time at approximately room temperature. The changes which occur in rubber in the ordinary process of freezing are generally attributed to crystallization.

In the accelerated freezing test described above the raw rubber did not pass through the opaque stage but remained transparent throughout the period of the test (4 hours). At $-60°$ C. the transparent rubber was so brittle that it could be shattered like glass by a light blow. Furthermore, it resumed its flexible condition when the temperature was allowed to rise to $-30°$ C.

SUMMARY OF RESULTS

(1) High and normal sulfur pure gum compounds became board-like and brittle within a few minutes when cooled at $-60°$ C., yet when tested at this temperature they had an elongation of over 500% and tensile strength of over 5,000 lbs. per sq. in.

(2) With decreasing temperature the two compounds gave increasing tensile strength and modulus and decreasing elongation.

(3) Relatively high combined sulfur, *i. e.*, up to over 8% on the rubber, was accompanied by a marked increase in hardness, even at temperatures no lower than $-30°$ C.

(4) A substitution of deproteinized rubber for smoked sheet appeared to give greater resistance to hardening at temperatures down to $-40°$ C.

(5) Unvulcanized, unmilled smoked sheet showed greater resistance to hardening on rapid cooling than the vulcanized compounds at all temperatures tested. This phenomenon, however, is not to be confused with that of ordinary frozen rubber, which is commonly observed at temperatures above $-30°$ C.

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STATIC AND DYNAMIC PROPERTIES OF RUBBER UNDER COMPRESSION *

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1. INTRODUCTION

Rubber undoubtedly possesses a number of unique properties which make it a particularly suitable accessory material for constructional purposes; *e. g.*, in elastic mountings, elastic couplings and dampers against torsional vibration on driving shafts. Its application to such uses, however, requires knowledge of other than the usual properties. Most of these are related to simple physical quantities such as modulus at a given elongation, hysteresis, permanent set and the like.

In § 2 will be discussed magnitudes that may be entailed in the cases in question. Relations existing between the various magnitudes will come up for consideration in the course of the discussion. Most of the problems involved have already received some attention. Some of the more important investigations into this subject will be dealt with in § 3.

Finally, the results of experimental work on the static and dynamic behavior of rubber under compression will be recorded in § 4.

2. GENERAL REMARKS ON ELASTIC PROPERTIES AND INTERNAL FRICTION.[1]

The vibrational behavior of rubber under compression may be treated in general terms as in the following example.

Figure 1 is a diagram of a machine with mass M, spring-mounted on a base with compliance c. Compliance is defined as deflection per unit of deflecting force.

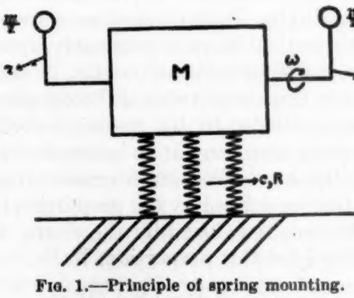

Fig. 1.—Principle of spring mounting.

The two masses, $m/2$, which revolve on the arms r at angular velocity ω, represent mass forces in the machine resulting from imperfect counter balancing.

Let the deviation from the balanced position be x, then the equation of vertical movement is:

$$\frac{Md^2x}{dt^2} + \frac{Rdx}{dt} + \frac{x}{c} = \text{(mass) force on } m \qquad \ldots\ldots\,(1).$$

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 59, pages 987-1000.

By hypothesis assume the frictional force to be equal to $\frac{Rdx}{dt}$, similar to the case of electrical resistance.

$$x = \frac{m\omega^2 r}{\sqrt{\left(\frac{1}{c} - M\omega^2\right)^2 + (\omega R)^2}} \qquad \text{........(2).}$$

is readily calculated from equation (1) for small deflections. For infinitely high frequency this becomes:

$$x_\infty = \frac{m}{M} r \qquad \text{........(3).}$$

So that the deflection is then independent of frequency.

When $\omega^2 Mc = 1$, the expression under the root becomes very small (almost the minimum[2]), in which case the system is said to be in resonance; x may then reach very high values; *e. g.:*

$$x_{\max} \approx x_{\text{res}} = \frac{m\omega r}{R}$$

$$x_{\text{res}} = \frac{x_\infty}{\omega Rc} \qquad \text{........(4).}$$

R was introduced as a constant, by hypothesis. Experiments have shown, however, that ωR is constant. Therefore, in analogy to the alternating current theory, ωRc is replaced by tan δ, and δ is called the angle of loss. Tan δ is a constant[3] so that equation (4) becomes:

$$x_{\text{res}} = \frac{x_\infty}{\tan \delta} \qquad \text{........(5).}$$

This equation makes it possible to determine the internal friction experimentally, for x_∞ can be calculated from m, M, and r with the aid of equation (3). All that is needed is to measure the resonance deflection, and tan δ can then be computed from equation (5). If at the same time the resonance-circular frequence, ω_0, is measured, c can be determined by this process of measurement, with the aid of the equation, $\omega_0^2 Mc = 1$. This method is quite commonly applied for the determination of c and tan δ. The compliance can, of course, be determined also by static compression tests. As a rule this static value of the compliance is greater than the so-called dynamic value as estimated by the resonance method.

The purpose of the spring mounting is to prevent vibration of the machine from being imparted to the base. The improvement resulting from the elastic mounting may therefore best be defined by the proportion in which the vibrational energy transmitted to the base is reduced by the elastic mounting. By approximation the following is found for this proportion, V:

$$V = \frac{\{(\omega/\omega_0)^2 - 1\}^2 + \tan^2 \delta}{1 + \tan^2 \delta} \qquad \text{........(6).}$$

Equation (6) shows that improvement occurs only if ω is higher than $\omega_0\sqrt{2}$. As usually tan $^2\delta \ll 1$,

$$V = (\omega/\omega_0)^4 \qquad \text{........(7).}$$

applies to high frequencies. It is necessary, therefore, for c to be such that the resonance frequency shall be as low as possible compared with the operational frequency. Necessarily therefore, as the machine starts up, the resonance point

is passed, in which case the deviation is limited by tan δ (see equation 5). This is the principal utility of internal friction in vibration insulation.

It is not possible to increase c without limit, because deflection f increases with c. For a spring with a straight compression curve, as in the case of certain steel springs:

$$\omega_0 = 1/\sqrt{Mc} = \sqrt{g/f} \qquad \ldots\ldots\ldots(8).$$

where g is the acceleration due to gravity. From this it is seen that ω_0 becomes low only when f is large so that, as a rule, good insulation demands large deflection. This holds good also, broadly, for non-linear springs.

The problem of insulation therefore demands types of spring of a predetermined compression and known tan δ. It must be possible also to calculate the static deflection under load. The question, therefore, is: what relations hold between c, δ, and deflection and the kind of rubber, the type of spring, the load, the frequency and so on? Another important question is: Does the deflection increase as time passes and on what does it depend?

Obviously, to answer the first question, compression tests must be applied to a spring of simple dimensions to determine Young's modulus, E, for the kind of rubber involved. E is deduced by definition from the slope of the compression curve as follows:

$$\left.\begin{aligned} E &= \frac{\Delta X}{\Delta f}\, h \\ E &= \frac{h}{Oc} \end{aligned}\right\} \qquad \ldots\ldots\ldots(9).$$

where ΔX = increase in the pressure (force per unit original surface O),
Δf = accompanying increase in the deflection,
h = initial height of the spring,
c = compliance.

It is tacitly understood that the rubber spring has a uniform cross-section at every level in the uncompressed state.

There are, however, certain complications to be reckoned with, for E is by no means a material constant in the case of rubber. E increases substantially with the pressure X. This is a generally known fact, for neither the tensile nor compression stress-strain curves are straight. Hooke's law, therefore, does not apply, and E is not a constant. A second complication is that E depends on the dimensions of the spring. This may be understood as follows: rubber owes its compressibility to the capacity of deflecting sideways. Rubber totally enclosed is, therefore, virtually incompressible. So its compliance will depend on the extent to which lateral deflection is possible. A massive cylindrical spring of diameter ϕ and height h will become barrel-shaped when compressed if special precautions are not taken. The ends of the cylinder are hampered in their lateral expansion and do not therefore contribute toward the compliance. Thus, a doubling of h produces more effect than a doubling of c. E will then diminish as h increases (with ϕ constant). Above a certain limit of h, which is approximately $h=\phi$, E is approximately independent of h, because the effect of the extremities is then relatively very slight. A parallel, generally known, fact is that a pressure spring, the ends of which are lubricated, is compressed further than the same spring, not lubricated, under the same pressure.

Hence, in the case of cylindrical rubber springs, E depends not only on the kind of rubber, but also on h, ϕ, and X. However, E will not depend on both

h and ϕ, but only upon h/ϕ. This we infer from the easily deduced rule that similarly shaped springs of the same homogeneous material under the same pressure X will undergo the same relative compression y. So E is the same for similarly shaped springs of the same material. Now h/ϕ is the magnitude which determines the shape and therefore E. So, according to equation (9), the compliance of a cylindrical spring is determined by:

$$c = h/\tfrac{1}{4}\pi\phi^2 . E(h/\phi, X, \text{kind of rubber}) \quad \ldots\ldots\ldots (10).$$

By theoretical considerations, equation (10) cannot be further simplified. Experimental examination will have to be used to show what the relation is between h/ϕ, X, and the kind of rubber on the one hand and E on the other.

The rule of conformity just mentioned applies in an analogous form to many cases; *e. g.*, to the rigidity modulus G, to the internal friction and to the dynamic values of E and G.

The last complication is the fact that the static value of the compliance of rubber is greater than the compliance with respect to vibrational forces (dynamic compliance). The ratio of these two values may in some instances amount to 2 or more. This phenomenon is often lost sight of. Yet it is rather important, as the dynamic compliance governs the position of the resonances and therefore the efficacy of the insulation. The value generally given in the literature for the ratio of static to dynamic compliance varies between 2 and 10. The question is discussed again in § 4.

Hitherto rubber has been regarded as vibration-insulating material. One application closely connected with this is shock-damping by means of rubber, as commonly applied in the automobile industry. The velocity of complete damping is an important matter for this purpose, so this is where internal friction is a primary factor. For shock absorption the non-linearity of the compression curve is very welcome, as thereby the spring is weak for slight compressions and yet remains elastic for very high loads.

The fact that rubber effects insulation without metallic contact appears as a distinct advantage in its favor as an insulating material. Accordingly, rubber is a better insulator against contact sound, *i. e.*, mechanical vibrations of audible frequency, than steel. Apart from this, there are concrete proofs of its good acoustic insulating properties. Theories discussed elsewhere[4] and substantiated by the experiments of Meyer and Keidel[5] show that the natural frequencies of insulating materials have an adverse effect on the insulation. The natural frequencies of rubber are far higher than those of steel springs; moreover, owing to the internal friction, this influence in the case of rubber will be less important.

For vibration insulation, rubber is often applied not for compression but for shear. In certain cases this is to be preferred, as the mechanism of construction is then often more elegant than with rubber under compression. At the same time the stability may be very great laterally, which again will be to the detriment of the insulation. With shear, it is as a rule a fairly easy matter to secure considerable deflection. Another advantage claimed is that there is less after-effect than with rubber under pressure. Otherwise the same problems arise, for here again the static and dynamic values of the rigidity modulus G, with accompanying internal friction, have to be determined.

Finally, the elastic behavior of rubber is affected by the temperature; indeed, temperature even has considerable influence on the internal friction. One technical application in which this effect of temperature is a very important factor is that of rubber in vibration absorbers to reduce the torsional vibration in driving shafts, as described by Föppl[6]. These absorbers are adjusted to the critical frequency

of the shaft. When resonance occurs, the absorber comes into action and converts the vibrational energy into heat. If the temperature of the rubber rises owing to internal friction, the resonance alters and the absorber consequently becomes less effective. As a matter of fact, particulars of the dynamic value of the rigidity modulus G and the extent of the internal friction are needed also for this application.

3. RESULTS OBTAINED BY OTHER INVESTIGATORS

One of the first serious investigations into the dynamic properties of vibration insulating materials is that made by Schmidt[7]. By mechanically aided optical means he projected small hysteresis loops undergone by the material while vibrating. From these data he calculated the dynamic compliance and the angle of loss. He found the static compliance from static compression tests. The magnitude of the angle of loss he found was of the order of 15°, which is exceedingly high for rubber. He gives 2—3 as the ratio of static to dynamic compliance. But he examined only one kind of rubber in one particular form, so his results are of limited importance for the general knowledge of the elastic properties of rubber.

Thum and Oeser[8] have published the results of an elaborate research into the determination of the dynamic compliance of cylindrical rubber springs. These results are given in the form of an empirical formula for the calculation of rubber springs. The only material constant they introduce beyond the dimensions ϕ and h is the hardness, which they measure, not in the spring itself, but in a sheet 6 mm. thick of the same material, with the aid of a Schopper hardness tester. Their method of determining the compliance is not purely dynamic. Although the empirical formula they give conforms only partly to the general expression given in equation (10), it nevertheless produces fairly good results for cylinders of moderate size. It is difficult to check the results, however, as the cylinder and test sheet must be of the same material and degree of vulcanization.

A very thorough investigation, especially into the internal friction, has been made by Steinborn[9]. Rubber cylinders of $\phi=5$ cm. and $h=9$ cm. were subjected in two ways to vibration, *viz.*, either by means of a resonance method approximately as described in § 2, or, alternatively, the cylinder was subjected to predetermined vibration of regulatable frequency. He determined the angle of loss from the resonance deflection or from temperature measurements, since heat is generated by internal friction and may be calculated from the rise in temperature. These differently determined values agree as well as may be expected[10]. The principal results are as follows:

(*a*) As had already been found by other authors[11], the angle of loss diminishes as the temperature rises.

(*b*) The angle of loss of various Buna grades is higher than that of natural rubbers of the same hardness. At a rough estimate the order of magnitude of the ratio is 1.5.

(*c*) If the hardness figures given by Steinborn are taken as a relative measure for the static compliance, the Buna grades are dynamically harder than the corresponding natural rubber grades. The same may be deduced from the stress-strain and compression curves he gives.

Cassie, Jones and Naunton determined the dynamic values for E and G and their frictional losses. They investigated the influence of the temperature, the elongation, the mix, antioxidants and vulcanization. The frictional losses on elongation reach a minimum approximately at optimum vulcanization. Antioxidants also have a distinct influence. They draw attention in particular to the phe-

nomena accompanying very small elongations. They demonstrated considerable losses, which were accompanied by short flexing life. Both were dependent in a marked degree upon the initial elongation.

The following may be cited also from the numerous publications on this subject. Wiegand and Snyder[12] pointed out the difference between static and dynamic Young's moduli, for which they held the thermodynamics of rubber (Joule effect) responsible. Morrison[13] described among other things static compression tests with lubricants and showed that stress-strain and compression curves have the same slope if calculated on the actual cross-section. Some interesting publications on practical applications have appeared by Hirshfeld and Piron[14], Hahn[15] and Keys[16]. Keys extended the uniformity principle mentioned in § 2 for rubber pressure springs. This extension, which can hold good only approximately, amounts to this: rubber pressure springs, the ratio of whose weighted surface to free lateral surface is the same, produce the same relative compression under the same surface pressure.

In conclusion may be mentioned the possibility of determining the compression curve of rubber by tests of two-directional elongations, *e. g.*, Sheppard and Clapson[17] and Russell[18]. The underlying principle is that the volume remains practically constant when compression or elongation is unidirectional.

4. RESULTS OF THE MEASUREMENT OF THE DYNAMIC AND STATIC BEHAVIOR OF RUBBER UNDER COMPRESSION

(a) *Apparatus and Method.*

The principle of the method[19] may be described as follows: The material under test is laid on a heavy steel plate, which is so fixed in the base that it cannot vibrate. A mass is placed on the material, vibrational forces of known magnitude and regulatable frequency being set up in the former, as shown in Figure 1. This mass can be weighted with steel compression springs up to several thousand kilograms, so the materials under test can be examined under pressure. The original method of measuring was based on equation (2). Measurements were made at frequencies below the resonance frequency. x was determined electrically, as was also the lag in phase between the mass force which gives rise to the vibration and the deflection x. c and δ were determined from these two observations and the frequency. This method was selected so as to be able to determine c and δ at any required frequency. As both c and δ proved to depend but little on the frequency, this lengthy method was abandoned in favor of a determination by the resonance method, as described in § 2. c and δ are therefore calculated from the resonance-frequency and resonance-deflection.

All measurements were made at room temperature, which on an average was $18 \pm 2°$ C. As all operations were with very slight deflections, increase in temperature, owing to internal generation of heat was a negligible factor.

All the specimens under test were in the form of massive cylinders, of which the h/ϕ ratio was equal to 1, $\frac{1}{2}$, or $\frac{1}{4}$.

(b) *Independence of the Amplitude.*

It had emerged from a number of tests that c and δ do not depend on the amplitude. An example is given in Table I. The frequency was consistently 1300 cycles per minute. Although x (in cm.) varies appreciably, δ is practically constant. Kosten and Zwikker[19] found no variation in c and δ, whereas the amplitude varied by a factor of more than 10. This effect seems to be generally applicable also to materials other than rubber[20].

(*c*) *Preliminary Measurements.*

A few preliminary measurements were made with rubbers of divergent compositions and vulcanization to find the limits within which the magnitudes varied. In these experiments the shape was constant, *viz.*, $h=\phi=5$ cm. The composition of the mixings used was as follows.

Mix A. F.L. Sheet 100, sulfur 5, zinc oxide 3, D.P.G. 1.

Mix B. F.L. Sheet 100, asphalt (Nurac) 8, zinc oxide 10, carbon black 44 (22 vol.-%), machine oil 2, stearic acid 2, D.P.G. 1¼, sulfur 3½.

The figures found are given in Table II, but it should be borne in mind that these are to be regarded only as indicating the order of magnitude.

TABLE I

INDEPENDENCE OF ANGLE OF LOSS OF THE AMPLITUDE

x	δ
0.0165 cm.	6°.50
0.0203 "	6°.55
0.0231 "	6°.64
0.0256 "	6°.51
0.0257 "	6°.51

TABLE II

ORDER OF MAGNITUDE OF YOUNG'S MODULUS AND ANGLE OF LOSS WITH VARIOUS MATERIALS

Material	δ	E_{dyn}
F. L. Crepe	2°.7	25.10^6 dynes p. sq. cm.
Mix A unvulcanized	4°.9	25.10^6 " " "
" vulcanized	2°.0	25.10^6 " " "
Mix B unvulcanized	8°.3	100.10^6 " " "
" vulcanized	7°.3	130.10^6 " " "

(*d*) *The Principle of Uniformity.*

In addition, the principle of uniformity was verified by measuring a large number of cylinders of mix A. The diameters were 1¼, 2½, 5 and 10 cm. Wherever possible, the three ratios for h/ϕ, ¼ or ½ or 1, were employed. The rubber was vulcanized for 240 minutes at 122° C. with 30 minutes' rise and 30 minutes' fall, to have material as homogeneously vulcanized as possible. The following figures were found:

Hardness	39 Shore durometer units.
Tensile strength	235 kg. per sq. cm.
Elongation at break	700%.

The results are plotted in Figure 2. The lines in this figure are the averages of the observations on cylinders of the same h/ϕ ratio. It was found that the elastic behavior of the springs tested depends only on the h/ϕ ratio, and is independent of the absolute dimensions, as explained in § 2.

The peculiar plotting is due to the fact that the compression curve of rubber resembles a hyperbola. Following Ariano[21], assume that the compression curve can be expressed as follows:

$$Xy-\alpha X+\beta y=0 \qquad \text{........(11).}$$

Then X/y and $\sqrt{E}$ are in linear relation to X. This appears to be approximately correct. Without differentiating diagrammatically, this allows a rough verification

of the extent to which E_{stat} differs from E_{dyn}. From the three lines X/y=function of X, using equation (11), have been calculated the three straight lines $\sqrt{E_{stat}}$=function of X. These latter lines are dotted in the dynamic part of the figure. So with these cylinders the difference between E_{stat} and E_{dyn} is inconsiderable. δ has a tendency to increase slightly with the frequency and the compression, although the course followed is not distinct. δ varied between 2° and 3°.

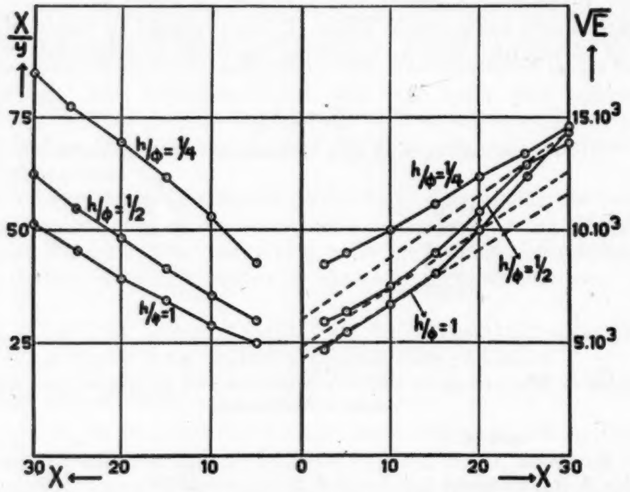

FIG. 2.—Static (left) and dynamic (right) behavior of mix A under pressure. X = mass load in kg. per sq. cm.; y = relative compression; E = Young's modulus in dynes per sq. cm.

TABLE III

CORRELATION BETWEEN δ AND E_{stat}/E_{dyn}

Mix	δ	E_{stat}/E_{dyn}
A	2°.1	0.9
A	2°.1	0.9
A	2°.4	0.9
A	4°.0	0.75
A	4°.6	0.5
A	4°.9	0.55
B	7°.4	0.38

(e) *Influence of Vulcanization with Mix A.*

Cassie, Jones and Naunton[22] have already found that the internal friction diminishes as optimum vulcanization approaches. This became clearly apparent in a number of tests applied to samples of Mix A of different shapes and vulcanization. At the same time, however, some relation proved to exist between E_{dyn}/E_{stat} and δ (Table III). This would denote that the two magnitudes depend on one and the same effect, which perhaps is connected with the plasticity. The last line in Table III refers to Mix B, but is of the same order as the figures for Mix A.

(*f*) *Various Mixes at Optimum Vulcanization.*

Investigations were carried out with three mixes at optimum vulcanization.

(i) Mix A. F.L. Sheet 100, sulfur 5, zinc oxide 3, D.P.G. 1, with the addition of Age-Rite 1, and 20 volumes of whiting or alternatively of zinc oxide.

The results of the whiting mixing, vulcanized to optimum, are given in Figure 3.

The difference between E_{dyn} and E_{stat} is inconsiderable, but it should be noted that this difference is diminished in the graph by the use of $\sqrt{E}$. The results for the zinc oxide mixing have not been given separately, as they practically coincide with the lines of Figure 3, but the difference between E_{dyn} and E_{stat} is a little greater. The angles of loss of the two mixes vary between 2.5° and 3.5° for the

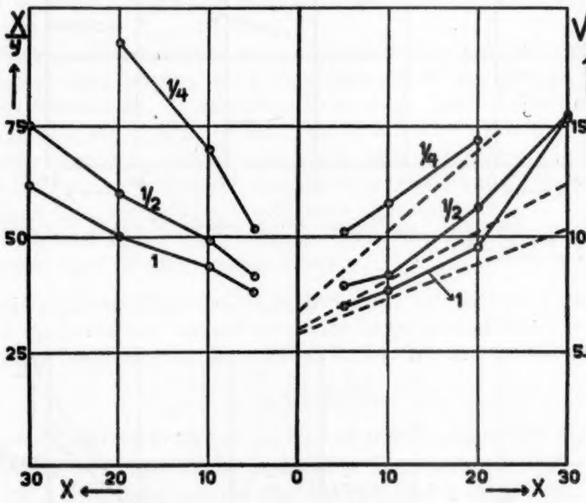

FIG. 3.—Static (left) and dynamic (right) behavior of mix A with 20% by volume whiting. X = load in kg. per sq. cm.; y = relative compression; E = Young's modulus in dynes per sq. cm.

whiting mix and 3°-4° for the zinc oxide mix. The hardness was 50 and 52 Shore units respectively.

(ii) Mix B consisted of F.L. Sheet 100, asphalt (Nurac) 8, zinc oxide 10, stearic acid 2, machine oil 2, sulfur 3½, Flectol B 1, A32 1, and carbon black (10% by vol.) 20. Vulcanization, 60 min. at 132° C. with 15 min. rise and 15 min. fall.

The results are shown in Figure 4.

Data for mix B are: hardness, 49½; tensile strength, 233 kg. per sq. cm.; elongation at break, 670%. The difference between E_{dyn} and E_{stat} is no longer inconsiderable; it is of the order of 50%. The angle of loss varies from 4° to 5°. As usual, a greater angle of loss corresponds with a greater difference between E_{dyn} and E_{stat}.

A mix like the previous one, but with 20% by volume of a non-reinforcing carbon, had virtually the same properties. Here again the angle of loss was 4° to 5°.

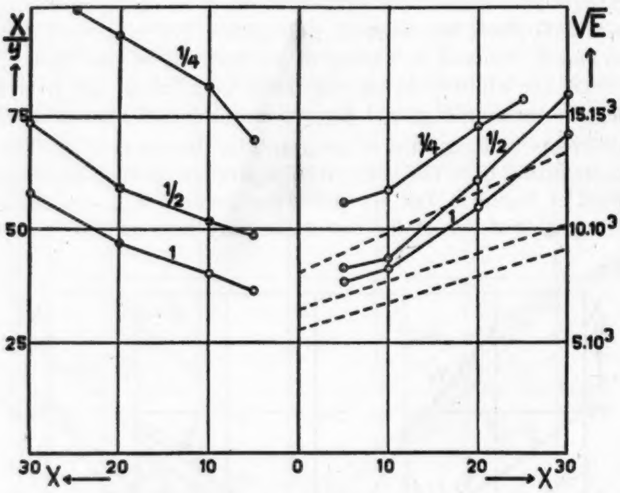

FIG. 4.—Static (left) and dynamic (right) behavior of mix B. X = load in kg. per sq. cm.; y = relative compression; E = Young's modulus in dynes per sq. cm.

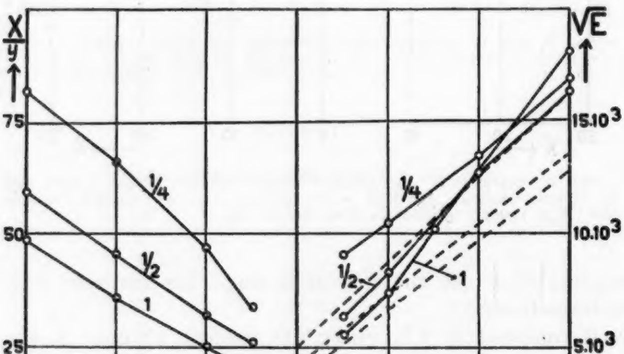

FIG. 5.—Static (left) and dynamic (right) behavior of Vanderbilt mix. X = load in kg. per sq. cm.; y = relative compression; E = Young's modulus in dynes per sq. cm.

(iii) In Figure 5 are given the results of a Vanderbilt mix of great durability, composed as follows:

F.L. Sheet	100
Sulfur	0.4
Captax	1
Zinc oxide	5
Age-Rite	1
Stearic acid	1
Tuads	$\frac{1}{4}$
Vandex	$\frac{1}{2}$

Vulcanization: 50 mins. at 127° C. with 15 min. rise and 15 min. fall. The hardness was 34 Shore durometer units, tensile strength 208 kg. per sq. cm., elongation at break 790%. The angle of loss was 2.5° to 3.5°, which agrees with the difference between E_{dyn} and E_{stat}.

The extent of the permanent set, as determined at the conclusion of the compression tests, after loading to a maximum of 30 kg. per sq. cm. for about 1 hour, was determined. It amounted to at most 2½%. Accurate measurements of this magnitude are difficult to make, but it is quite certain that a large angle of loss generally occurs in those mixes which exhibit high permanent set. Crude rubber, in the form of cylinders pressed out of crepe, was an exception, as it had a low angle of loss, yet could not withstand high loads.

(*g*) *Optimum Load of Compression Springs.*

In § 2 the problem of insulation against vibration was fully discussed. It was found that the lower the various resonance frequencies, the better the insulation. The resonance frequency for the vertical translation movement was:

$$\omega_0 = 1/\sqrt{Mc}.$$

It would not be correct to choose the highest possible figure for M, as c diminishes very substantially for high loads, as shown in Figures 2 to 5. Where $\sqrt{E}$ increases linearly with X, it may be inferred that the best load is equal to the opposite of the portion which is cut off by this line from the negative X axis. The order of magnitude of the most effectual loads is 10 kg. per sq. cm. for soft kinds of rubber and 30 kg. per sq. cm. and higher for harder grades. It is clear from Figures 2 to 5 that springs of small h/ϕ must be more heavily loaded than springs of large h/ϕ. Finally, it should be pointed out that a spring of, say, $h/\phi = 1$ cannot be loaded unlimitedly. There is a tendency to buckle which, as the load increases, is manifested at first by declining stability in a horizontal direction, until eventually the buckling load is reached. In the case of rubber grades of 30 to 40 Shore durometer units' hardness, this limit is as low as about 8 kg. per sq. cm. A greater load is permissible, provided the stability in a horizontal direction be artificially enhanced by, for example, auxiliary springs.

(*h*) *The Nature of Internal Friction.*

In the cases considered above, the internal friction was invariably closely connected with concepts such as plasticity and permanent set. In a certain sense it is justifiable to regard the angle of loss as a measure of the imperfect elasticity of the rubber.

The cause of internal friction in materials like sponge rubber, cork and felt is an altogether different one. Its origin lies, in our opinion, in a completely different

property, *viz.*, the porosity. Here the friction is caused by air resistance in the pores. An investigation has already been made[23] into the damping of vibration by sponge rubber. It would take us too far to deal with this matter fully here, but the main results may be summarized as follows. The angle of loss is far from being independent of frequency. For high frequencies the movement of air in the pores is too slow to be able to contribute towards the angle of loss. At lower frequencies, however, the angle of loss passes a certain maximum which, in the case of a particular sponge rubber tested, was at 700 r.p.m. The maximum amounted to 20°, which is unattainable with massive rubber. Above this frequency the losses decrease substantially. Hypotheses regarding air friction in the pores bear out the results very satisfactorily.

CONCLUSIONS DRAWN FROM THE EXPERIMENTAL WORK

1. Young's modulus, E, calculated from static tests, is smaller than the modulus calculated from dynamic tests. The ratio of E_{dyn} to E_{stat} as a rule lies between 1 and 2.

2. Properly vulcanized mixes rich in rubber exhibit a small mechanical angle of loss, slight difference between E_{dyn} and E_{stat}, and low permanent set.

3. Mixes containing, say, 20% by volume of filler, display, even with optimum vulcanization, a greater angle of loss, accompanied by greater disparity between E_{dyn} and E_{stat}, and greater permanent set. The same applies to undervulcanized mixes rich in rubber.

4. E_{dyn} is independent of the frequency. Even at the lowest frequencies at which measurements can be made (250 r.p.m.) the difference between E_{dyn} and E_{stat} remains constant.

5. The angle of loss has a tendency to increase with the frequency and the load. Expansion of surface at higher pressure is probably a factor in this case.

6. Popularly expressed, it may be said that plasticity, static hysteresis, angle of loss, permanent set and relation between dynamic and static Young's moduli are closely allied concepts, so that the angle of loss may be accepted as a measure of the elastic imperfection of rubber.

In conclusion, the author wishes to express his gratitude to the Rubber-Stichting for permission to publish the investigation described in the foregoing pages, to C. Zwikker, Professor of Physics at the University College of Technology, Delft, for his valuable supervision, and to A. van Rossem, Director of the Research Department of the Rubber-Stichting, for his assistance and the interest he has so kindly displayed in this work.

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DYNAMIC EVALUATION OF DAMPING AND DURABILITY OF RUBBER COMPOUNDS *

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DYNAMIC EVALUATION

1. *General.*

The application of rubber is steadily increasing in all fields. There is a growing demand for tires in all countries as a result of an increasing motorization of traffic with higher speed on better roads. The structural application of rubber in mechanical engineering, especially in motor cars for vibration damping, is another field for the successful application of rubber.

In all these applications the dynamic stress (by alternating loads) on the rubber compounds predominates over the static stress.

The static methods of testing rubber compounds, as for instance the measurement of the tensile strength, hardness or resilience, are not sufficient to evaluate compounds that undergo dynamic stress as in the tire carcass or in vibration absorbers. It is therefore necessary to develop apparatus that makes possible the evaluation of rubber under dynamic stress over long periods of time. During the test the conditions of load must be known correctly.

The purpose of these tests is:

(*a*) To develop compounds destined for dynamic stress, especially for vibration-absorption or for the tire carcass;

(*b*) To reveal the basic physical properties necessary for the calculation of vibration problems;

(*c*) To compare natural and synthetic rubber compounds according to their dynamic characteristics.

The physical properties of the vulcanizates to be measured during such fatigue tests are:

(*a*) Damping or hysteresis (the rate of energy absorption);
(*b*) Dynamic modulus;
(*c*) Dynamic drift during the fatigue test;
(*d*) Durability;
(*e*) Bonding.

2. *Apparatus.*

The apparatus to be described in this paper consists of an eccentric weight (Thumscher Schwinger) (see Figs. 1 and 2), mounted on a shaft which is driven by a direct-current motor through a flexible coupling. The two bearings of the shaft are mounted in a casing resting on four flat springs. This casing oscillates under the influence of the rotating weight in a horizontal direction, thus translating an alternating load to the cylindrical rubber sample (*e. g.*, 40 mm. high and 40 mm. in diameter), which is mounted between the casing and a stationary dynamometer

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in the shape of a tube. A steel spring mounted on the other side of the casing gives the static load on the sample. For the fatigue test there may be chosen either tension, tension-compression or compression.

(*a*) The alternating load can be regulated by the eccentricity of the rotating weight or the speed of the motor;

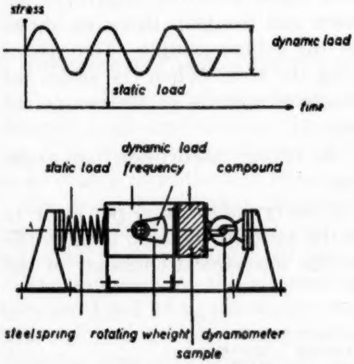

FIG. 1.—Apparatus for determination of damping.

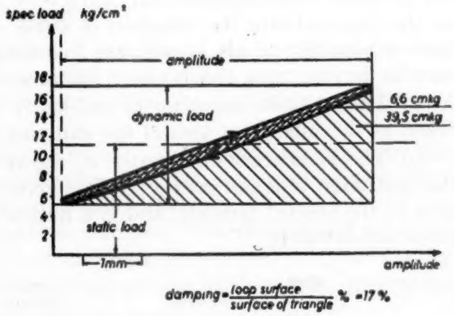

FIG. 3.—The dynamic damping loop.

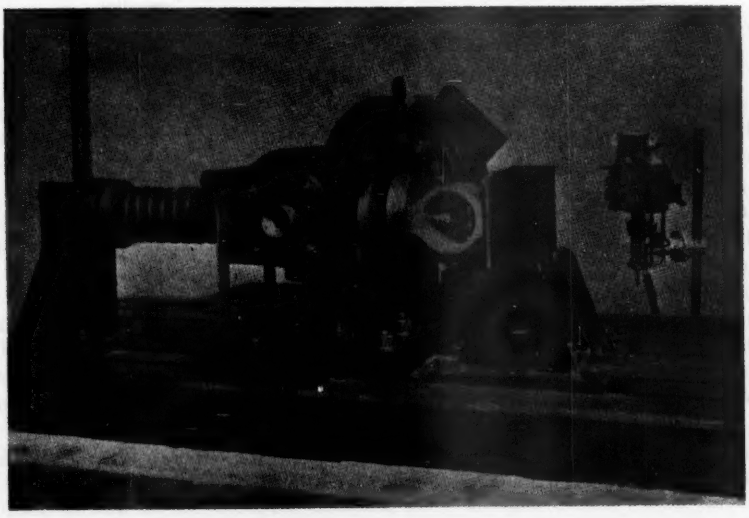

FIG. 2.—Apparatus for determination of damping.

(*b*) The static load can be changed by means of the steel spring;

(*c*) The frequency of the alternating load may be altered by the speed of the motor.

The amplitude of the oscillation and the values of the static and dynamic loads are measured during the test by means of two mirrors, one of them being mounted on the casing; the other one is placed within the tube-shaped dynamometer. A

beam of light from an arc-lamp is deflected by either of these mirrors and describes on a screen the dynamic hysteresis loop of the rubber compound under test. This damping loop may be copied or photographed on a film.

3. *Analysis of the Test Results.*

Figure 3 reproduces a hysteresis loop that was taken with the apparatus described. The compression form of test was chosen and the loop therefore shows the dynamic stress-compression characteristic of the rubber sample. The arrows on the loop indicate the direction of stress during the test. When the scales for load and amplitude are known, the following elastic properties of the compound may be derived from the dynamic hysteresis loop:

(*a*) The ***absolute damping*** in cm.-kg., *i. e.*, the energy absorption per cycle, taken as the superficial area of the damping loop.

(*b*) The *percentage damping, i. e.*, the ratio of energy absorption per cycle to the maximum input of energy; this is given by the ratio of the loop area to the area of the shaded triangle, and is a measure of the mechanical efficiency of the vibration-damping.

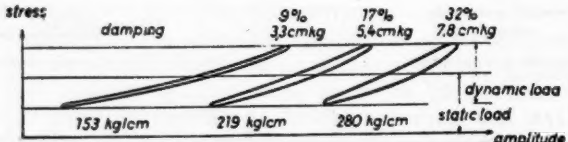

FIG. 4.—Damping of rubber compounds.

(*c*) The ***dynamic modulus*** in kg. per cm., *i. e.*, the deflection per unit load, which is given as the ratio of the maximum dynamic stress to the maximum deflection.

(*d*) The ***dynamic drift*** in cm. during the fatigue test with constant static and dynamic load (which is to be regulated during the test). It is given as the path which the centre of the damping loop describes on the zero line of the alternating load during the fatigue test.

(*e*) The ***durability*** of the compound. If the sample is destroyed during the fatigue test, the durability of the compound under the given load conditions is exceeded. By stating the relation between the life period of the sample and the corresponding dynamic load conditions, it is possible to find the load which the sample can withstand for an infinite time, *i. e.*, the durability of the compound.

(*f*) The ***dynamic bonding***. If the durability of the test sample exceeds the dynamic bonding, there will be obtained a measure of the adhesion of the compound to metals or other materials under dynamic conditions.

4. *Film of the Damping (Hysteresis) Loops.*

A short film shows three characteristic damping loops for vulcanizates with small, medium and large damping. The inclination of the loop indicates the modulus of the composition, and from the size and shape of the loop one may easily deduce the damping value of the compound. Table I shows the absolute damping, the percentage damping and the dynamic modulus of the three characteristic mixes. Figure 4 gives a comparison of the damping loops for the same mixes.

TABLE I

	Buna S. I	Buna S. II	Buna S. III
Absolute damping, cm.-kg.	3.3	5.4	7.8
Percentage damping (%)	9	17	32
Dynamic modulus (kg. per cm.)	153	219	280

TEST RESULTS

5. *Influence of Physical Factors on Damping.*

The method of testing described makes it possible to study the influence of different load conditions on the elastic qualities of the mixes, especially on damping. The smaller the influence of the load conditions, the broader the conclusions to be drawn from the test results.

The tests showed that the percentage damping is not much influenced by the amount of static or dynamic load applied or by the frequency, thus being a characteristic dynamic quality of the compound itself.

The influence of the alternating load on damping was determined for loads between 4 and 18 kg per sq. cm., static load and frequency being constant (Fig. 5). The absolute damping increases with increasing alternating load; the percentage damping does not change.

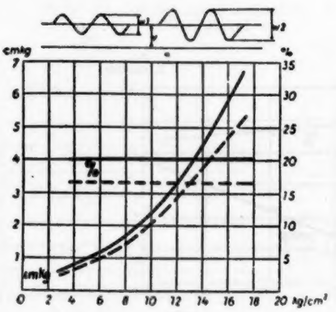

FIG. 5.—Damping as a function of the alternating load.

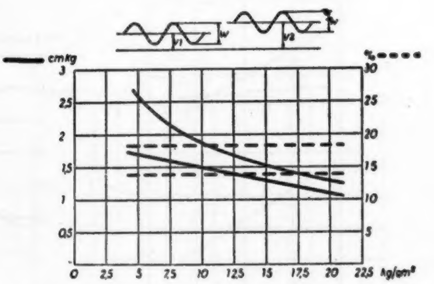

FIG. 6.—Damping as a function of the static load.

The influence of the static load on damping was determined for loads between 5 and 20 kg. per sq. cm., alternating load and frequency being constant (Fig. 6). The absolute damping decreased with increasing static load; the percentage damping shows not much change.

The influence of frequency on damping was determined between 0.5 and 1,000 cycles per minute, static and dynamic loads being constant. The percentage damping as well as the absolute damping show a slight increase with increasing frequency (Fig. 7).

For the accuracy of the test results it is very important to know the influence of temperature on damping. In most cases damping changes very much with temperature. Damping means energy absorption, which implies the conversion of mechanical energy into heat. The magnitude of damping will, therefore, be different according as the loop is taken at the start of the fatigue test or after the final temperature has been reached. To study the influence of temperature on damping, the temperature of the sample was measured by means of a thermocouple, and values of temperature and damping were taken from the start until

the final temperature was reached. Figure 8*a* shows temperature and damping as a function of time. From these curves it was possible to plot damping as a function of temperature, as Figure 8*b* shows for different compounds. On account of the different temperature coefficients of the diverging damping-curves, a comparison of various mixes will show different results according as it is made at normal or at higher temperatures. This result is important for the comparison of tire compounds.

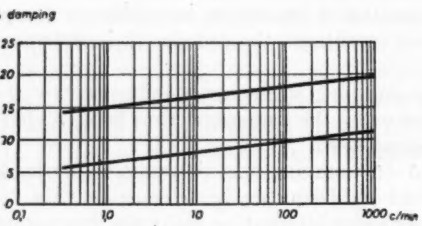

FIG. 7.—Damping as a function of frequency.

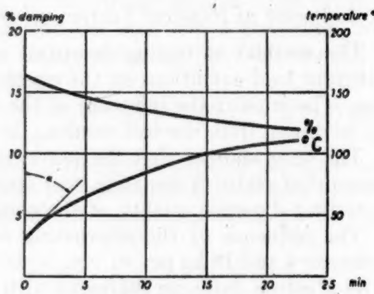

FIG. 8A.—Damping and temperature as functions of time.

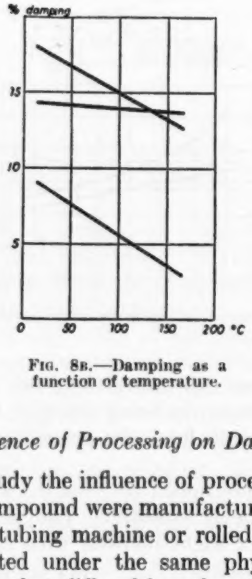

FIG. 8B.—Damping as a function of temperature.

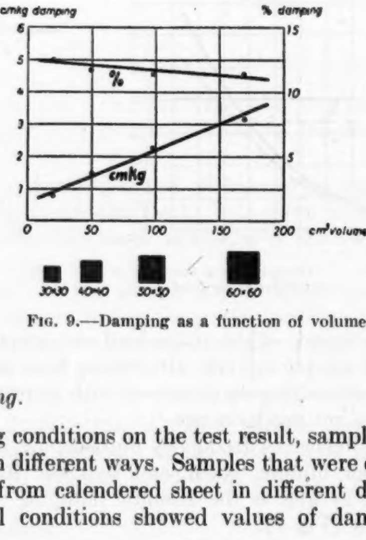

FIG. 9.—Damping as a function of volume.

6. *Influence of Processing on Damping.*

To study the influence of processing conditions on the test result, samples of the same compound were manufactured in different ways. Samples that were extruded from a tubing machine or rolled up from calendered sheet in different directions and tested under the same physical conditions showed values of damping or modulus that differed less than 10%.

To determine the influence of the volume of the sample on damping, cylinders of 30×30, 40×40, 50×50 and 60×60 mm. were tested under constant conditions of static and dynamic load and frequency. The absolute damping increased with increasing volume of the sample; the percentage damping showed only a slight decrease (Fig. 9).

Figure 10 shows the influence of vulcanization on damping. Undervulcanization resulted in higher damping compared with normal or overvulcanization.

7. Applicability of the Test.

(*a*) *Comparison and Evaluation of Compounds.*—The test can be used for the evaluation of ingredients of a compound with respect to their influence on damping. Figure 11 shows the percentage of damping as a function of the percentage of sulfur contained in a compound. Damping decreases considerably with increasing percentage of sulfur in the mix. For other technological reasons only a small section of the curve has practical significance, but the tendency is characteristic and interesting.

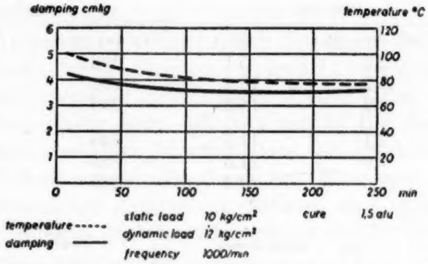

FIG. 10.—Damping as a function of time of vulcanization.

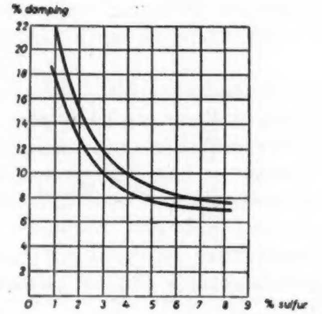

FIG. 11.—Damping as a function of sulfur.

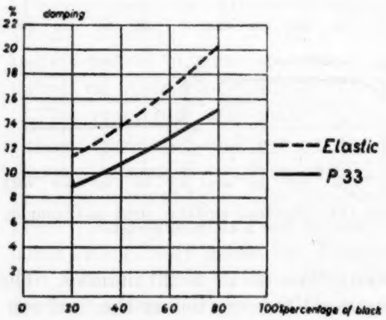

FIG. 12.—Damping as a function of percentage of carbon black.

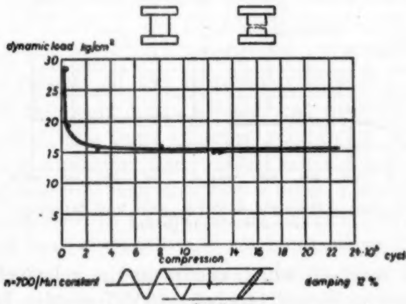

FIG. 13.—Durability of rubber compounds.

In another case the influence of the percentage of carbon black on the damping of the compound was tested, and the curves show (Fig. 12) an increase of damping with increasing percentage of black.

Table II shows a comparison of a variety of compounds used for the tread and carcass of different types of tires. The lowest values of damping belong to racing-tires of which, on account of the high speeds, a minimum of heat development and therefore of damping is desired.

(*b*) *Durability.*—By determining corresponding values of the alternating load and the time for the first cracks to show on the surface of the sample under the influence of this stress, a curve as shown in Figure 13 is obtained. The asymptote of the curve gives the durability of the compound for the conditions of the fatigue test. If samples are used which are cemented to metal plates and the durability of the rubber compounds exceeds the bonding, the test results in a determination of dynamic bonding.

(*c*) *Dynamic Evaluation over Longer Periods.*—Often the question arises how compounds behave under dynamic stress over longer periods of time. To study this case the fatigue tests were extended over 400 hours, and damping loops were taken every hour. Absolute and percentage damping, dynamic modulus and drift were determined, as the curves of these values were drawn as functions of time. Figures 14*a* and 14*b* show two characteristic types of mixes with respect to their dynamic behavior. In the one case (Fig. 14*a*) the damping, modulus and drift changes but slowly after the "final" (equilibrium) temperature of the test

TABLE II

Sample		Damping Abs. (cm.-kg.)	Damping %	Dynamic modulus, (kg. per cm.)
18	Carcass.	2.6	5.1	196
33	"	5.2	10.6	226
47	"	8.2	18.2	256
30	Tread.	4.1	11.5	346
54	"	7.0	21.3	386
74	"	10.5	29.4	346

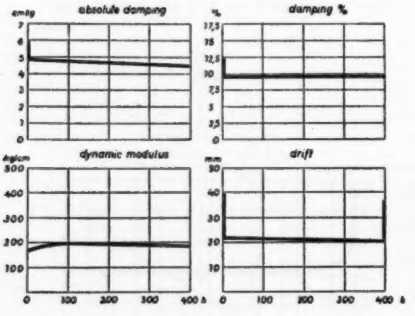

FIG. 14A.—Dynamic modulus, drift and damping over a 400-hour period.

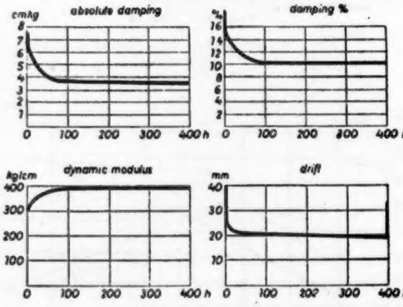

FIG. 14B.—Dynamic modulus, drift and damping over a 400-hour period.

is reached, which occurs in the relatively short time of 15 to 20 minutes. The mix of Figure 14*b* behaves differently. It requires 100 hours before the final condition of the material is reached. During this period the compound seems to undergo structural changes, for the final geometrical shape of the sample is reached much earlier (as the drift shows) than the values of damping and modulus reach their constant values. The final increase of height at the end of the drift curve indicates the recovery of the sample 1 hour after the removal of the load.

SUMMARY

The method described in this paper makes possible the dynamic evaluation of rubber and rubber-like compounds. It allows the measuring of the dynamic damping (hysteresis) loop during the fatigue test, and may be applied not only to small rubber samples but to larger objects such as vibration absorbers and whole tires.

The apparatus renders valuable service in developing compounds of natural and synthetic rubber that undergo dynamic stress.

THE INTERNAL FRICTION OF VULCANIZED RUBBER *

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Although the elastic properties of rubber have been extensively studied, the viscous properties have scarcely been investigated. Thus we know very little about the damping properties of rubber.

In general, the laws which determine the mechanical behavior of any material are of a simple form only as long as we consider very small deformations and very small speeds of deformation. Under these restrictions, the elastic behavior of a plasto-elastic body will be given by the Hooke-Hencky law, and as regards the plastic behavior Newton's law will be followed. For slow torsional oscillations of small amplitude, these two laws may be combined into the classical expression for damped oscillations, and from this the following expressions for the internal friction or viscosity η and for the shearing modulus γ can be deduced:

$$\eta = \frac{4LI}{\pi R^4 \tau} \log_e \frac{\phi_1}{\phi_2} \quad \ldots (1) \qquad \gamma = \frac{8\pi LI}{R^4 \tau^2} \quad \ldots (2)$$

Here the piece of material is supposed to be in the form of a long thin cylinder (length L, radius R), having a moment of inertia I and oscillating freely with a pseudo-period of τ sec., ϕ_1 and ϕ_2 being two successive amplitudes. The observation of a torsion-pendulum will thus furnish all the required quantities.

This pendulum was made up in the following way. Cylindrical threads of rubber (prepared and put at our disposal in a most obliging way by A. van Rossem) about 45 cm. long and 0.3 cm. in diameter, were suspended in a water-jacketed vertical tube. The lower end of this tube was closed by a large T-shaped piece. The lower end of the thread was clamped to a thin rod, 20 cm. long, which could swing freely inside the T-piece and bore a small brass weight at either end and a little mirror at its centre. The image of a linear-filament lamp, after reflection in this mirror, was observed on a scale 120 cm. away. The amplitude, ϕ, of torsional oscillations of the thread inside the evacuated apparatus could thus be measured down to some minutes of angle, while the period was easily determined by timing successive passages through zero.

Experiments with slightly as well as with highly vulcanized rubber showed that the internal frictions of these substances increase very rapidly, even at quite small deformations (2°), while the moduli of elasticity increase much less. Thus Hooke's law applies correctly to rubber over an interval of deformation many times larger than does Newton's law. Therefore the observed "logarithmic decrements" for amplitudes between 2° and 10 minutes had to be extrapolated to zero amplitude, and this quantity was used in equation (1) to calculate the internal friction of rubber, which was found to be of the order of several million c.g.s. units. These experiments show that viscosity is only slightly affected by vulcanization. On the other hand, modulus of elasticity shows a marked decrease

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 66, pages 985-986.

as the degree of vulcanization increases. The behavior of rubber at small deformations is thus the opposite of that which is found at large deformations or under high stresses (several kg. per sq. mm.).

It was found also that the viscosity of rubber, between 12° and 45° C., is nearly independent of temperature, quite unlike that of substances such as pitch. In this respect vulcanized rubber resembles not so much a liquid as another "high polymer," *i.e.*, vitreous quartz.

THE USE OF THE PENDULUM IN RUBBER TESTING *

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INTRODUCTION

During the past few years considerable interest has been shown in the use of pendulum methods for the study of resilience properties of rubber compounds. We feel therefore that an account of the development and use of the pendulum method in the Dunlop Rubber Co.'s laboratories will prove of general use. In this country the period from 1918 witnessed a rapid extension in road transport, carried at that time almost exclusively on solid tires. With this development the performance of heavy vehicles improved considerably and tires were operated under the increasingly severe conditions, both with respect to speed and load. It is well known, that if a solid tire is operated under sufficiently severe conditions it is no longer able to dissipate the heat developed within it, and its temperature rises until eventually an explosion or the familiar "blow-out" occurs. This phenomenon, of course, results from the fact that rubber is not perfectly elastic. When transmitting energy it does not release all the energy supplied to it. Some of the energy is always absorbed and appears in the rubber in the form of heat; the faster the energy is supplied, the greater is the increase in temperature.

Rubber technologists in those days were relatively poorly equipped with testing instruments and, in consequence, little was known of the internal properties of rubber. The usual physical tests were restricted to those which evaluated the tensile and hardness properties of the material, together with the early forms of apparatus used for investigating resistance to wear, cutting and aging. For the study of the overheating problem, the only reliable method of evaluating the resistance of solid tire compounds available at this time was a machine test in which a solid tire was run on a drum under conditions of high speed and load to produce an overheating failure and its temperature observed throughout its life by periodic insertion of a thermojunction. While such a method was direct, it had a number of obvious disadvantages: it was far too slow, it was very expensive, and even if the tires were not destroyed it rendered them unfit for use on the road. In an endeavor to eliminate the destructive element of the test, a first form of pendulum was developed in which a section of a complete solid tire was struck by a mass of metal, the tire being suitably located in respect to the pendulum. In this way we were certainly able to derive useful information concerning power consumption and hardness in solid tires, but the necessity for a complete tire however imposed severe limitations on the scope of the test and these, with the growing realization of the importance of accurate temperature control, which was impracticable with such large masses, led to the search for a more compact and more generally applicable type of instrument. In the laboratories the only type of hysteresis test then available was one in which a rubber ring was alternately stretched and allowed to retract at a uniform rate, an autographic record being made of the stress-strain relationship. In this way a hysteresis loop, the area of which is a measure of the energy absorbed in the work cycle, was

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 87, pages 830-848.

obtained. When considered, however, in the light of the requirements of a suitable test for tire compounds, it was soon evident that such a test suffered very severe drawbacks. Compared with the stress cycle which the rubber in the tire undergoes with each revolution of the wheel, the cycle is much too long. To compare with solid tires running at approximately 20 m.p.h., the cycle should be completed within about one-fiftieth of a second. In order to get a measurable hysteresis loop the rubber has to be stretched to a considerable elongation, whereas in the case of the tire the dimensional change is relatively small. Further, owing to the slow rate of elongation and the large surface area of the sample, much of the heat developed during elongation is dissipated before retraction begins. In a tire a far larger proportion of such energy is used by the tire in returning to its original shape after deformation. The large strains involved in stretching a ring result also in the rubber acquiring a permanent set which does not normally occur in practice.

Attempts to reduce the period of the working cycle to that required were only partially successful, and the method was eventually abandoned. Some attention was given also to an impact test in which a steel ball was dropped from various heights on to a flat test-piece of rubber and the resilience and hardness were determined by measuring the rebound and penetration of the ball. The problem of making the necessary measurements with sufficient accuracy resulted in a technique which was not adaptable to the rapid examination of large numbers of routine samples.

Finally we adopted the method of testing by means of the pendulum described below, which was designed to reproduce the cycle of changes which occurs when a solid tire is run under load at about 20 m.p.h.

We cannot claim any originality in the use of the pendulum for resilience and hardness measurements. It has been in use in other industries for many years and its use in the rubber industry is described in a paper as far back as 1919. Our adoption of this type of test for rubber compounds dates back some 17 or 18 years, during which time, of course, it has been subject to a number of minor improvements. Once the experimental requirements are realized, there is no particular difficulty in designing a pendulum to yield information on resilience and dynamic hardness, but its application to the determination of energy consumption under constant load conditions such as obtain in a tire constitutes in our view a novel contribution to the subject.

OUTLINE OF THE METHOD AND DEFINITIONS

The apparatus consists essentially of a compound pendulum carrying a steel ball which strikes a sample of rubber when allowed to fall under gravity. Suitable mechanisms are provided, as will shortly be described, to measure the rebound of the pendulum and the penetration of the steel ball into the rubber at maximum indentation. These measurements, together with the various mechanical constants of the pendulum, provide us with material to calculate the following characteristics of the rubber under test.

1. *Resilience.*—We define resilience as the ratio of the energy returned to the pendulum to its initial energy when it is allowed to fall on to the test sample from a standard height. We believe that the resilience of rubber compounds as measured on the pendulum gives an excellent indication of state of vulcanization and is naturally at a maximum at the best state. Resilience must always be measured for a fixed height of fall since it depends on the amount of energy supplied. It is also sensitive to temperature variation at room temperatures.

2. *Indentation at Standard Force.*—This is the maximum indentation corresponding to a standard force on the rubber sample. It may be defined also as the dynamic hardness and can be regarded as a measure of the running deflection of the tread of a tire made from the same mixing. In contrast to the resilience, the indentation at standard force does not vary to any great extent with temperature, within moderate limits.

3. *Power Loss.*—This is defined as the energy absorbed during one cycle by the rubber at standard force, as a result of its internal friction.

4. *Standard Force.*—The definitions of indentation and power loss require amplification of the term "standard force." At first sight it might be thought that the indentation associated with the resilience determination and the energy loss implicit in the resilience itself would provide the necessary information on a particular rubber compound. But resilience is determined under conditions of constant energy supply, and the actual load on the rubber at the instant of maximum indentation, can vary within wide limits depending on the nature of the rubber compound under test. In the case of a tire running on the road, however, the load is constant and to provide a true parallel the penetration and power loss as measured on the pendulum must be determined under constant load conditions. In other words, they must be measured under such experimental conditions that the force on the rubber at maximum indentation has a predetermined value. This force is known as the standard force.

The derivation of indentation and power loss thus involves the use of an indirect method of arriving at the standard force. The procedure employed consists in obtaining two curves, known respectively as the power loss and indentation curves. In the former energy losses are plotted against the ratios of corresponding force at maximum indentation to indentation. In the latter, penetrations are plotted against these ratios. From these the power loss and indentation at standard force are deduced. Reference to the description of the experimental procedure and to the theory developed in the appendix will render this apparently complicated process clear. The analysis is based on two assumptions, the first of which is justified by experiment, and the second, while obviously not rigorously true, is sufficiently so not to affect results to any appreciable extent. We are satisfied in practice that over a wide range of compounds the errors involved are very small.

DESCRIPTION OF THE APPARATUS

The pendulum is made from sheet duralumin and is strengthened by a length of angle iron running parallel to its leading edge. It is suspended from a spindle mounted on ball bearings projecting from the main support of the pendulum, which is a very stiff girder. The energy of the pendulum is transmitted to the rubber block under test by means of a 1 in. steel ball fixed to the leading edge of the pendulum at the centre of percussion in the manner shown in Figure 4. The mounting of the steel ball also carries part of the indentation mechanism. The displacement of the pendulum is measured along a horizontal wooden scale reading in centimeters. As the pendulum has to be dropped from various heights depending on the type of rubber under test, a release mechanism is provided. This is mounted on a slide on a horizontal bar parallel to the scale and a few inches below it to the right of another mechanism, the rebound machanism, which enables the operator to read the rebound of the pendulum to a high degree of accuracy.

The Release and Rebound Mechanisms.

The nature of these is clearly seen in Figure 3. The essential feature of the release mechanism is a spring-loaded catch which can rapidly be moved out of position when it is desired to release the pendulum without absorbing any of the energy of the pendulum, and accurately returned to its initial position when the pendulum moves into position for further "drops." The rebound mechanism consists essentially of two bent levers capable of small movement which are pivoted to the base plate and fitted with return springs. On pulling the left hand lever, its other extremity, which carries a small cam free to rotate against a small friction force, comes into the path of the pendulum. If this action is performed between the passing of the pendulum on the impact swing and the repassing on the rebound, the edge of the beam, *i. e.*, the projecting edge of the angle iron bracing, will hit this cam. Provided that the slide is set roughly to the correct position, this being done by sight on the first rebound from any given height, the cam will be pushed up to the point of highest rebound. After the pendulum has rebounded ten or twelve times this height will be found to be constant and as there is no actual contact with the beam at this stage none of the energy of the pendulum is absorbed by the rebound mechanism. To determine the actual scale-reading for such a rebound the cam is locked in position by moving the second lever, which was previously mentioned, to the right. Then the pendulum is raised till it comes into contact with the cam and the scale-reading noted. Parallax is avoided by sighting the forward blackened side of the beam as a black line. To facilitate this reading the remainder of the beam is painted white over a considerable length as shown in the illustration (Fig. 2).

Indentation Mechanism.

The penetration of the steel ball into the rubber block is measured directly by means of a dial screw-gauge giving readings to one-hundredth of a millimeter, which is mounted through an electrically insulating packing to the body of the pendulum as shown in Figures 4 and 5. The foot of the gauge projects in such a manner as to come into the path of the remainder of the indentation mechanism mounted on the pendulum with the steel ball as previously mentioned. This part consists of a spring-loaded plunger which, when it makes contact with the foot of the dial gauge, completes an electrical circuit through the pendulum, the pendulum support, the gauge and a pair of telephones, the necessary current being supplied by a small battery. In practice the gauge is adjusted by the operator until contact, judged by the sound in the telephones, is just not made when the steel ball is at maximum indentation.

Sample.

The sample is a block of rubber 2 in. sq. by 1 in. thick taken from a solid tire or vulcanized in a suitable mould. In the case of solid tires, considerable experience is required before a sample with parallel sides and of uniform thickness can be made, but this problem does not apply to moulded samples. When it is desired to test samples from laboratory or mill-mixed rubber it is usual to test four samples of each compound at four different states of vulcanization, and these are made by using four moulds each containing one sample of each of four mixings. Vulcanization is effected in a small autoclave pan which permits of one mould being withdrawn with a minimum of cooling to the remaining ones.

Sample Holder.

The sample holder is mounted in the correct position, with respect to the striker ball, on the girder from which the pendulum is suspended. It consists of a circular holder 1 in. deep into which the sample blocks will just fit. A circular plate with suitable thermal insulation on the outside is pivoted at one point on its circumference and is thus capable of rotation to cover the front of the block holder as

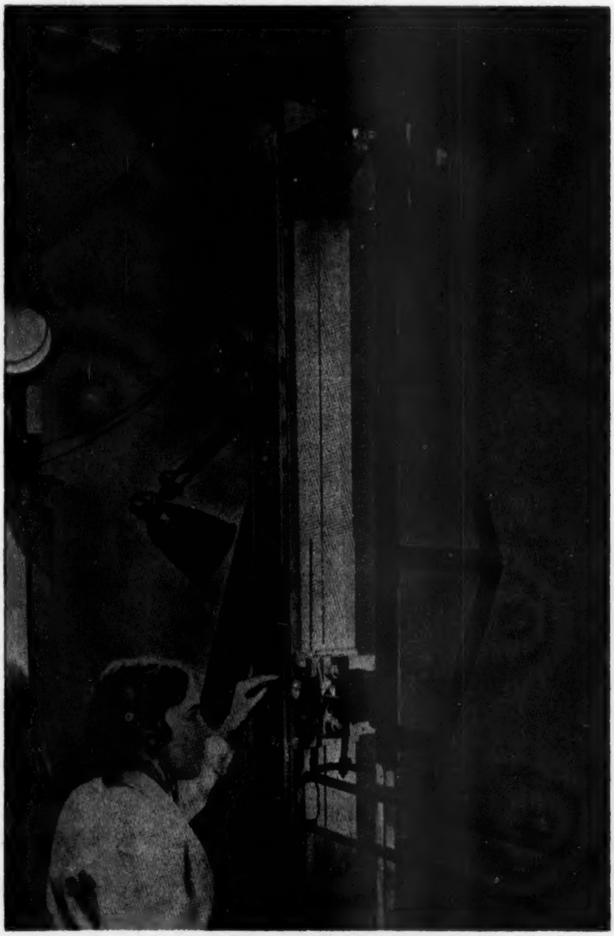

FIG. 1.—General view of pendulum. The pendulum is at rest with the striker ball in contact with test block.

required. A stop is fitted to keep the plate in position during test. This plate naturally has a central hole just large enough to admit the striker ball. To keep the rubber block rigidly in position during the test the plate is provided also with two bow springs of suitable dimensions.

The sample holder at the back is in contact with a block of iron which has a mercury cup at the top to take a thermometer and which can be heated to the desired temperature with a gas jet, placed beneath it.

Temperature of Test.

This factor is of the greatest importance, and unless careful attention is given to it, it is impossible to derive any results from the pendulum which have any value. The samples to be tested are kept for at least 1½ hours in a thermostatically controlled over maintained at 50° C., which is conveniently near the pendulum.

Apart from the fact that a better control of temperature is possible at temperatures considerably above surrounding air temperature, this temperature was chosen because it was found that at 50° C. the resilience value was much less sensitive to temperature variations than at room temperatures. At higher temperatures the resilience is less sensitive still to temperature variations, but there are a number of reasons why such temperatures cannot be adopted in practice. The samples have to be transferred from the oven to the sample holder on the pendulum by hand, and 50° C. is quite high enough for the hands of the operators. In addition, there would be a greater heat loss from the sample on its way to the pendulum at higher temperatures and, in spite of the gas heating of the sample holder, it would be difficult to maintain uniform temperature distribution throughout the block. In practice we find that at 50° C. a temperature variation of $\pm 1°$ C. does not cause sufficient variation to affect results appreciably. To obtain this temperature in the block while it is under test, the gas jet is adjusted till the thermometer is at about 52° C. We find however that a more reliable indication of temperature conditions is obtained by inserting a standard block from time to time during a run of tests. If the temperature is correct, its resilience will not change.

METHOD OF TEST

Two operators are needed, one to attend to the release and rebound mechanisms and the other for the indentation apparatus. The test blocks having been stored in the oven at the correct temperature for a sufficiently long period and the sample holder on the pendulum being also at the correct temperature, a block is transferred from the oven to the holder as quickly as possible and the cover fitted into position. The pendulum is then raised and held by the release mechanism. In extreme cases the height may be as great as 85 cm. for very soft blocks or as little as 50 cm. for very hard ones. In each case four separate heights of drop are employed; for instance, 85, 80, 75 and 70, or 65, 60, 55 and 50 cm. If, as in the first example, a drop from 60 cm. is not included, an additional drop has to be taken from this point as this information is necessary for the determination of the resilience.

A drop of 60 cm., for example, means a drop from a height corresponding to an angular displacement of the pendulum the tangent of which is the horizontal displacement of the beam of the pendulum, *i. e.*, 60 cm., divided by the vertical distance between the pivot of the pendulum and the scale.

The pendulum being set in position, the micrometer is set at approximately the correct reading and the pendulum released. If the operator hears a click in the telephones the foot of the gauge is screwed away from the striker ball; if no click is heard it is screwed towards the ball. With successive drops of the pendulum at short intervals, the gauge reading corresponding to the maximum indentation of the steel ball is quickly arrived at. It is found that the penetration gradually increases till about the sixth drop of the pendulum and then remains constant. Before the actual penetration corresponding to any given height of fall can be determined, however, it is necessary to know the gauge reading corresponding to

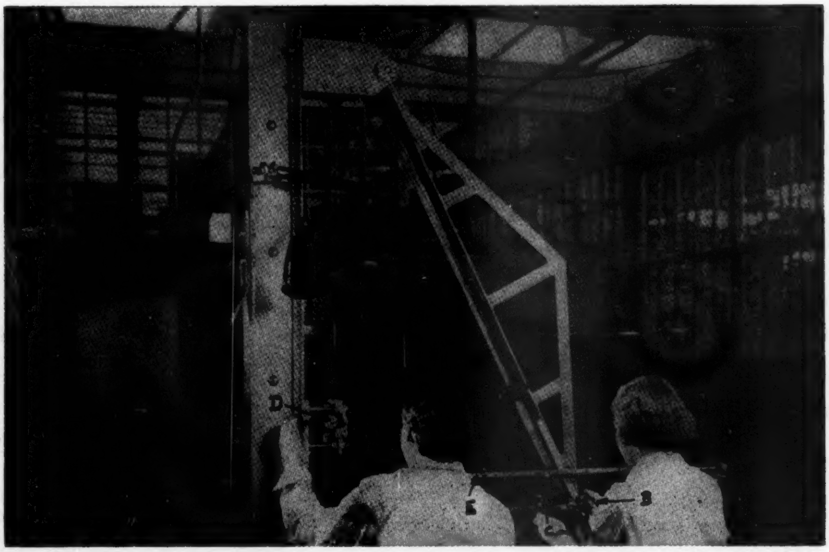

Fig. 2.—Another general view of pendulum. The operator on the right is about to release the pendulum, while the operator on the left is preparing to take the maximum indentation gauge reading. B, release mechanism; C, rebound mechanism; D, dial gauge for measuring maximum indentation; E, horizontal scale for measuring pendulum displacement.

Fig. 3.—Close-up of release and rebound mechanisms. With the rebound mechanism retracted the operator is about to release the pendulum. B, release mechanism; C, rebound mechanism.

zero indentation. This is obtained by holding the pendulum ball gently against the block so that it just makes contact with it and adjusting the micrometer until the plunger first makes contact with it. To eliminate any possibility of deformation of the block when carrying out this operation, a small metal disc, about 3 cm. in diameter and 1 mm. thick, is inserted between the block and ball and due allowance is made for its thickness when reading the gauge. The difference between the gauge reading at maximum indentation and at zero gives the penetration corresponding to this particular height of fall. As this operation of obtaining the zero gauge reading is likely to affect the temperature of the block the maximum indentation readings are always taken first.

Meantime the other operator has been resetting the pendulum after each rebound and, when the block has reached its steady state, measuring the rebound, as has already been described in the section dealing with the release and rebound mechanisms. When the operators have become experienced, the time taken for the dozen or so drops that are necessary at each height becomes surprisingly short and is limited only by the period of the pendulum.

In this way penetration and rebound readings are taken corresponding to four different drops of the pendulum at intervals of 5 cm. along the scale. From the theory of the method given in the appendix it will be seen that, as the force at maximum indentation is largely dependent on the hardness of the samples, this range of heights will vary with the type of rubber being tested. Provided this range is correctly chosen, there will be no necessity for extrapolation of the power loss and indentation curves. Today it is no longer necessary to leave the choice of the range of heights to the operator, for the accumulated experience of a number of years has enabled us to construct a slide rule by means of which, given the indentation and rebound corresponding to the drop of 60 cm., the range of heights necessary to give the standard force midway can be accurately selected.

DERIVATION OF RESULTS

(*a*) *Resilience* (*Res*).

In every case this is determined for a height of fall corresponding to a scale reading of 60 cm. The value of $(1-\cos\theta)$ at this point is 0.1177 and the ratio of the value of $(1-\cos\theta)$ for the rebound to 0.1177 gives the resilience, by definition equal to $\left(\frac{E_1}{E_2}\right)$.

(*b*) *Power Loss* (*PL*).

The power loss at the standard force is derived by plotting the energy losses against the force values. These are obtained by taking the energy values corresponding to each drop and rebound of the pendulum from tables. Their difference gives the energy loss (E_1-E_2) and their sum divided by the indentation the corresponding force value $\frac{(E_1+E_2)}{S}$. The energy loss corresponding to the standard force line (0.204) is the power loss. This operation will be clear from reference to the set of typical examples given at the end of this section.

(*c*) *Indentation* (*I*).

This is derived in a similar manner by plotting the penetration values against the corresponding force values.

FIG. 4.—Close-up of steel striker ball in contact with surface of the test block. A, steel striker ball; D, dial gauge for measuring maximum indentation; F, spring-loaded plunger for indentation measurements; G, gas heating for sample holder; H, sample holder.

FIG. 5.—Fig. 4 from a different angle.

Typical Examples. (See Table I.)

The actual plotting operations are simplified by the use of a black-board suitably marked out with vertical and horizontal lines, which is placed on a table. For each test the ordinates and abscissæ are chalked in and the points plotted by placing rubber discs in the correct positions. A flexible rule is then held above the discs to give a smooth curve passing through the four points, and the values of power loss or indentation corresponding to standard force values are noted.

FIG. 6.—View from the back of pendulum showing the operator placing a test block in the sample holder.

APPLICATIONS

We will now consider the advantages of such a method of testing, a number of which will no doubt have become obvious during the course of the description.

In the first place the test is an extremely simple one and thus does not depend on highly skilled operators for its efficient operation. We find that the junior class of laboratory assistants is able, after a very brief period of introduction to the test, to work it quite satisfactorily and obtain results with the required accuracy and rapidity. Secondly, in contrast to so many of our laboratory tests on rubber which are of the destructive type, it has the great advantage that the samples are available for repeat tests should any doubt arise as to the accuracy of the initial results. The test-pieces take up little space and can be conveniently filed away in great numbers for future reference, if necessary. In the Schopper and Scott tests one of the great drawbacks has always been the necessity of carrying large stocks of samples in the event of future tests being necessary.

TABLE I

Drop	Rebound	Gauge reading, mm.	Energy of fall	Energy of rebound	Indentation, mm.	Sum of energies $(E_1 + E_2)$	Energy loss $(E_1 - E_2)$	Force value $\frac{(E_1 + E_2)}{S}$	Results		
									Res.	I.	P.L.
1. *Solid tire.*											
—	—	1.98	—	—	—	—	—	—	—	—	—
60	51.8	—	—	—	—	—	—	—	—	—	—
55	47.7	9.64	1014	0789	7.66	1803	0225	234	776	7.15	18.0
50	43.6	9.20	0858	0672	7.22	1530	0186	212	—	—	—
45	39.4	8.70	0711	0558	6.72	1269	0153	189	—	—	—
40	35.2	8.16	0574	0452	6.18	1026	0122	166	—	—	—
2. *Pneumatic tread.*											
—	—	1.52	—	—	—	—	—	—	—	—	—
65	51.2	11.67	1344	0895	10.15	2239	0449	220	670	9.70	39.0
60	47.7	11.22	1177	0789	9.70	1966	0388	203	—	—	—
55	43.9	10.67	1014	0681	9.15	1695	0333	185	—	—	—
50	40.1	10.06	0858	0577	8.54	1435	0281	168	—	—	—
3. *Cushion rubber.*											
—	—	1.92	—	—	—	—	—	—	—	—	—
60	56.9	—	—	—	—	—	—	—	—	—	—
80	74.0	17.10	1868	1637	15.18	3505	0231	232	915	14.15	14.5
75	70.0	16.63	1692	1517	14.71	3209	0175	218	—	—	—
70	65.8	16.07	1517	1372	14.15	2889	0145	204	—	—	—
65	61.4	15.48	1344	1223	13.56	2569	0121	198	—	—	—

NOTE.—The underlined figures in column 3 (gauge readings) are the gauge zeros.

Then, again, when one considers the wide margins of experimental error which are almost invariably associated with tests on rubber, the accuracy of the pendulum test is surprising. Unskilled operators should be able to measure rebound to within ±0.1 cm. and penetration to ±0.05 mm., while skilled operators have no difficulty in working to closer limits. This means that results are correct to within one-half of 1% or less, which is a very small permissible error in routine testing. As a result of these narrow limits it is possible to follow changes in rubber compounds which could not readily be observed by other methods. It should be noted, too, that when the indentation and rebound mechanisms are in their final positions after a number of impacts, none of the energy of the pendulum is absorbed in making the necessary observations. There are of course losses due to friction in the pendulum pivot bearings and to windage, but these are very small in comparison with the losses in the rubber.

Apart from its simplicity the pendulum requires very little in the way of subsidiary equipment, for, with the exception of a small power supply for the oven, and gas for the sample holder, it is quite self-contained. Also, as a result of its

simplicity there is very little in the instrument to go wrong and it can be operated for long periods without need for attention. These are very desirable features in a laboratory instrument which is in continuous use.

But in our opinion one of the greatest advantages of the pendulum method of testing lies in the fact that we are able rapidly and accurately to evaluate properties, of rubber compounds which are of great importance in tires. In this respect its superiority over the Schopper type of test is obvious. The value of the pendulum in laboratory routine and factory control testing is further enhanced in that the properties which it evaluates are particularly sensitive to change in state of vulcanization and small variations in compounding. Experience has shown that the optimum vulcanization can be selected by this test with much greater certainty than by consideration of tensile strength and modulus. In some cases the lowest power loss does not coincide with the highest resilience, owing to progressive hardening with further vulcanization. This applies particularly to compounds containing little or no accelerator and correspondingly large proportions of sulfur. We explained at the beginning of this paper that the pendulum test was developed at a time when hysteresis losses in solid tires presented a very real problem demanding a speedy solution, and there was in existence no suitable instrument to guide us in an investigation. To-day the solid tire is rapidly disappearing from the roads, but we find that the value of the pendulum is increased rather than diminished. Rubber is more and more finding applications under conditions which involve the transmission or absorption of large quantities of energy, and in the selection of suitable compounds for such purposes the pendulum still remains one of the most valuable instruments we possess. For many years the capabilities of pneumatic tires for dissipating heat generated in service were quite adequate. But recent improvements in road construction and in the performance of motor vehicles have brought the tire manufacturer to a point where he can no longer afford to ignore the hysteresis properties of both tread and casing compounds. The reverse properties are needed in rubber compounds designed for absorbing energy, as in engine and machinery mountings, and the pendulum test has been of great service in this field. The use of the pendulum has also been extended to the evaluation and selection of compounding ingredients and raw rubbers. For this purpose, the test is regarded as supplementary to the usual stress-strain data, the additional information being frequently of considerable significance.

We will now give some tables showing how pendulum properties are affected by various factors, including state of vulcanization, types of carbon black, volume loadings of gas black, type of accelerator and raw rubber. From these we hope that the use of the pendulum in compound development and routine control will be made quite clear.

In Table II the resilience maxima and the power loss minima are clearly defined. The low resilience values and high power losses associated with gas black mixings are shown up in a striking manner.

The mixings in Table III were vulcanized at a pressure of 30 lbs. per sq. in. (134° C.) and the pendulum properties selected at the optimum vulcanization for each loading of gas black. With increase in gas black content there is a sharp fall in resilience of the mixing and a corresponding increase in power loss. There is also a progressive hardening as the black content of the mixing is increased.

The mixings in Table IV were vulcanized at 30 lbs. per sq. in. (134° C.) with the exception of the HMT mixings, which were vulcanized at 40 lbs. per sq. in. (141° C.). The pendulum properties were selected at the optimum vulcanization in each case.

It will be noted that in some cases the addition of stearic acid to a gas black mixing has a beneficial effect on resilience and power loss; in others the reverse.

The effect of replacing gas black by lamp black is very marked, for while the former affects resilience and power loss adversely, the fall in resilience is not nearly so pronounced with lamp black. In regard to power loss it is seen that with some

TABLE II

RATES OF VULCANIZATION WITH DIFFERENT BLACKS

Base Mix.

Rubber	100
Sulfur	3
Di-o-tolyguanidine	1
Zinc oxide	5
Black	15—Volumes.

Vulcanization	Resilience	Indentation	Power loss
(a) *Lamp black.*			
15–50 at 30 lbs. per sq. in. (134° C.)	841	11.9	20.5
75 " "	864	10.7	16.1
100 " "	878	10.4	13.3
125 " "	883	10.5	13.0
150 " "	878	10.8	13.5
(b) *Gas black.*			
15–50 at 30 lbs. per sq. in. (134° C.)	730	13.8	44.7
75 " "	764	12.4	36.3
100 " "	782	11.7	32.7
125 " "	779	11.4	31.0
150 " "	770	11.6	32.8
(c) *Acetylene black.*			
15–50 at 30 lbs. per sq. in. (134° C.)	815	12.4	22.4
75 " "	833	10.5	19.2
100 " "	845	9.6	17.0
125 " "	850	9.0	15.3
150 " "	847	9.4	16.0

TABLE III

EFFECT OF VARIOUS LOADINGS OF GAS BLACK ON PENDULUM PROPERTIES

Base Mix.

Rubber	100
Sulfur	3
Zinc oxide	5
Di-o-tolyguanidine	1
Gas black	As shown.

Gas black loadings (volumes)	Resilience	Indentation	Power loss
5	862	13.7	22.7
10	815	12.5	26.5
15	778	11.5	30.3
20	730	10.6	33.9
25	680	9.6	36.5
30	635	8.6	39.8

accelerators the addition of lamp black results in values which are actually lower than those of the unloaded mixings.

The mixings in Table V were vulcanized at 30 lbs. per sq. in. (134° C.) and the pendulum properties selected at optimum vulcanization in each case. The plasticity values of the raw rubber are plastimeter readings obtained after mixing, low plasticity values indicating hard rubbers.

TABLE IV

EFFECT OF ACCELERATORS ON PENDULUM PROPERTIES

Base Mix.

Rubber	100
Sulfur	3
Zinc oxide	5
Accelerator	1

Property	Accelerator	Base mix	Base mix + 50 gas black	Base mix + 50 gas black, + 2 stearic acid	Base mix + 50 lamp black
Resilience	DPG.	887	640	605	817
	DOTG.	901	630	617	825
	HMT.	825	637	609	791
	Grasselerator 808.	892	588	607	828
	MBT.	843	538	607	779
	Ureka.	889	632	635	851
Indentation	DPG.	15.15	8.35	8.70	8.20
	DOTG.	14.20	8.45	8.50	8.05
	HMT.	16.60	8.20	7.90	9.20
	Grasselerator 808.	14.55	10.80	8.65	8.15
	MBT.	17.00	9.95	7.90	9.70
	Ureka.	15.45	9.40	7.90	7.90
Power Loss	DPG.	19.0	35.5	43.5	17.0
	DOTG.	16.0	38.5	41.5	15.5
	HMT.	34.0	34.0	36.0	21.0
	Grasselerator 808.	18.5	59.0	47.5	15.5
	MBT.	30.0	61.5	40.0	24.0
	Ureka.	19.5	44.0	36.0	12.5

TABLE V

EFFECT OF RAW RUBBER ON PENDULUM PROPERTIES

Base Mix.

Rubber	100
Sulfur	4
Mercaptobenzothiazole	0.4
Stearic acid	0.8
Zinc oxide	50

Source of rubber	Pendulum properties: Resilience	Indentation	Power loss	Optimum vulcanization, (min.)	Plasticity
Estate 1 (*a*)	878	12.8	17.0	50	518
(*b*)	870	13.2	19.0	50	491
(*c*)	876	12.9	17.5	50–75	499
Estate 2 (*a*)	889	12.3	15.0	25–50	496
(*b*)	876	12.4	17.0	50–75	494
Estate 3	861	13.3	20.5	75	522
Estate 4 (*a*)	870	12.8	18.5	75	486
(*b*)	838	13.6	24.5	75	544
(*c*)	864	13.4	20.0	75–100	519
Estate 5	857	13.7	21.5	50–75	543
Estate 6 (*a*)	870	12.9	18.5	75	511
(*b*)	864	14.1	21.5	100	517
(*c*)	857	13.4	21.0	100	512
Estate 7	838	13.8	25.0	100	521

The results show that in general hard raw rubbers yield somewhat harder vulcanized products with higher resilience values. They are also faster vulcanizing.

Recent years have seen the development of other methods of evaluating the hysteresis properties of rubber compounds and a number of these have been made and used in our laboratories at Fort Dunlop. These confirm the accuracy of the pendulum results.

We wish to express our indebtedness to the Directors of the Dunlop Rubber Company for permission to publish this paper, particularly to A. Healey, the Birmingham Works Director, who was responsible for the original design of the pendulum, and to colleagues who have provided us with necessary information.

APPENDIX

A. *Theory of the Pendulum.*

In line with the theory of the rigid pendulum we take the following notation:

Mass of moving part............................ $=M$
Distance of centre of gravity from axis............. $=h$
Acceleration due to gravity...................... $=g$
Angle between raised pendulum and its position at rest $=\theta$
Potential energy of pendulum at angle θ............ $=Mgh(1-\cos\theta)$.

Let us assume that the force (F) acting on the pendulum at maximum indentation (S) is proportional to some power (x) of this indentation.

Then:—$F=kS^x$, where k is a constant...............................(1).

The energy required to produce this indentation is given by:

$$E=\int_0^S FdS=k\frac{S^{x+1}}{x+1} \quad \text{......................(2).}$$

In the pendulum test, however, some energy is required to overcome the internal friction of the rubber, and the actual potential energy of the strain is less than the kinetic energy of the pendulum which produces the indentation.

If we assume that half the energy is lost on the inward journey of the pendulum, the energy (E) required to produce the indentation will be the mean of the initial (E_1) and final (E_2) energies of the pendulum,

i. e.,
$$E=\frac{E_1+E_2}{2}$$

If E_a and E_b are the energies of the pendulum corresponding to heights of fall a and b respectively, we have from equation (1):

$$E_a=k\frac{S_a^{x+1}}{x+1}$$

and
$$E_b=k\frac{S_b^{x+1}}{x+1}$$

$$\therefore \quad \frac{E_a}{E_b}=\left(\frac{S_a}{S_b}\right)^{x+1} \quad \text{..........................(3).}$$

In this equation E_a, E_b, S_a and S_b can all be ascertained by experiment and thus x can be determined. Over a wide range of heights of fall it is found to be very

nearly 1.55 for hard and soft rubbers. We are thus justified in assuming that the force acting on the pendulum at maximum indentation is proportional to some power of the indentation.

By eliminating k from equations (1) and (2) we obtain the equation:

$$E = \frac{FS}{x+1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4).$$

In practice it is required to find the energy lost when a standard force is applied and removed, as this is what takes place in a tire running on the road under load.

When a convenient value is given to F, $\frac{E}{S}$ will be constant as x does not vary. It thus remains to determine the value of S for which $\frac{E}{S}$ has a predetermined value. This is the indentation at standard force.

The power loss is obtained in a similar manner and is the energy loss at constant force, *i. e.*, $(E_1 - E_2)$ when $\frac{E}{S}$ is a constant.

Determination of the Energy of the Pendulum.—The potential energy of the pendulum corresponding to any scale reading is calculated as follows:

The vertical fall of the centre of gravity (h) from displacement θ to the position of rest, *i. e.*, at the bottom of the swing, is $h(1-\cos\theta)$, and the potential energy at displacement θ is $Mgh\ (1-\cos\theta)$.

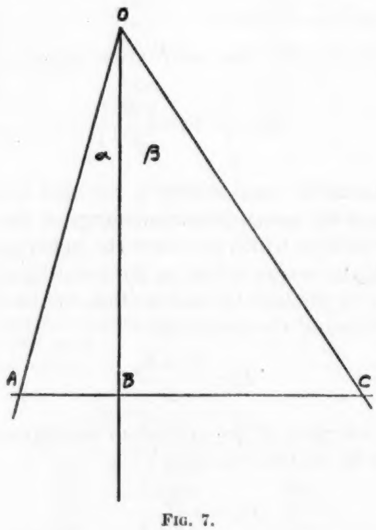

FIG. 7.

The value of $(1-\cos\theta)$ is conveniently found by the following method:

Let OA, Figure 7, be the equilibrium position of the pendulum when hanging freely, OB the vertical, OC the position of the pendulum at displacement θ.

Then: $$\theta = \underline{/AOB} + \underline{/BOC} = \alpha + \beta.$$

But, $$\tan\alpha = \frac{AB}{OB}, \text{ and } \tan\beta = \frac{BC}{OB},$$

i. e., α and β are known in terms of measured distances, and thus, θ and $(1-\theta)$ are known.

To reduce to a minimum the amount of calculation which the operator has to do in obtaining results, a set of tables is provided giving the values of cos θ corresponding to scale readings of the displaced pendulum at intervals of every millimeter from 30 cm. to 85 cm.

The factor Mgh is not included in the tables, since it is more convenient and leads to greater simplification to use arbitrary units and incorporate it with another constant, *i. e.*, the $\frac{1}{2}$ in the mean value of (E_1+E_2) in the expression for the standard force (Appendix B). It will be noted, too, that decimal points are not included in the tables and in obtaining results. For convenience, the values for power loss are always multiplied by 1,000. Resilience is usually given to three figures without the decimal point.

A section of the tables is appended.

	0	1	2	3	4	5	6	7	8	9
60	1177	1180	1183	1187	1191	1194	1198	1201	1204	1207
61	1210	1213	1217	1220	1223	1227	1230	1233	1237	1240
62	1243	1246	1249	1253	1256	1259	1263	1266	1269	1273
63	1276	1279	1283	1286	1290	1293	1297	1300	1304	1307
64	1310	1313	1317	1320	1323	1327	1330	1334	1337	1341
65	1344	1347	1351	1354	1357	1361	1364	1368	1372	1375

B. Method of Obtaining the Standard Force Line (0.204).

The standard force is taken as 100 kg. and $x+1$ as 2.55 since $x=1.55$.

In the pendulum test at Fort Dunlop, energy readings are in units of 377.1×10^6 ergs.

Thus from equation (4):

$$\frac{E}{S}=\frac{F}{x+1}$$

i. e.,

$$\frac{E\times377.1\times10^6}{S}=\frac{100\times1{,}000\times981}{2.55}$$

To simplify calculations, as has already been mentioned, the sum of the initial and final energies of the pendulum is taken instead of the mean.

Hence our expression becomes:

$$\frac{E\times377.1\times10^6}{2\times S}=\frac{100\times1{,}000\times981}{2.55}$$

or

$$\frac{E}{S}=0.204.$$

THE VARIABILITY OF RAW RUBBER *

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INTRODUCTION

It has long been recognized that commercial grades of raw rubber show variations in properties which are of importance to manufacturers. The term variability is applied to the collective variations in properties which the user is unable to assess, at the time of purchase, by the methods of testing at present available.

The producer should obviously reduce variability as far as it is economically possible. How is this to be done?

As soon as bulk supplies of plantation rubber began to appear in the European market from the East, complaints were made by manufacturers about variation in quality.† These complaints were based on the fact that the first-grade raw rubber which had been used up to that time, "fine hard Para" from the Amazon region, did not suffer from this defect, or at least suffered to a much smaller extent.

Soon afterwards Boutaric compared samples of *Hevea brasiliensis* rubber of these two types, giving figures based on the formula: $C = \frac{A \times R}{2}$, where A is the elongation at break and R is the tensile strength.

The following conclusions were drawn from this study:

(1) The mean value of C is approximately the same for plantation and fine Para rubbers.

(2) The difference between the maximum and minimum values of C, in suitable units, is 318 for plantation rubber and 239 for fine Para.

It is evident that these data are only of partial value since they concern only two properties of the rubber, extensibility and tensile strength. They enable us, however, to demonstrate by actual figures that the variability of plantation rubber is much more pronounced than that of Para rubber.

Much has been written on the causes of this variability, and emphasis has been laid on causes for which the planter is not responsible. It is considered desirable, at any rate from a technical point of view, to draw attention to another aspect of the problem.

The causes of variation in the quality of raw rubber should be divided into two groups:

(1) those which are due to variations in the quality of natural latex as it arrives at the estate factory;

(2) those which are due to the processes used in preparing raw rubber, from the filtration of the latex to the packing of the rubber.

VARIATIONS IN THE PROPERTIES OF NATURAL LATEX

There are numerous causes of variation in quality. In order to eliminate these as far as possible from a practical and economic point of view, careful planters now use methods which would appear difficult to improve materially, at any rate in the case of ordinary and not monoclonal plantations.

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 11, pages 82-35.

† See, for example, various articles in the *India-Rubber Journal* of 1909 and 1910.

Many of these causes of variation in quality are present also in the case of the Amazon rubber, and from personal experience it can be stated that the *seringueiro*, even one who works most skilfully and conscientiously, does not achieve a better standardization of his product than the big eastern plantations.

We must therefore seek elsewhere for the explanation of the differences in variability which exist between the two types of raw rubber.

VARIATIONS IN THE PREPARATION OF RAW RUBBER

The table below summarizes the essential differences in the two methods of preparation.

The brief notes in the table are intended to show that in the preparation of raw rubber there are some essential differences in the two metehods employed. These should provide a sufficient explanation for the variation in quality. It appears probable, so far as variations due to the method of preparation are concerned, that the methods which are universally used throughout the Amazon basin are effective in reducing the variability in quality of raw rubber to a minimum. These methods comprise the action of smoke on uncoagulated latex, and slow and progressively increasing pressure, which affects a steady compression of the mass and converts the plastic coagulum into highly elastic rubber. It should be noted also that this gradual transformation is possible only if the rubber is thoroughly and uniformly impregnated with volatile antiseptic substances before coagulation takes place.

From a practical point of view it appears to us that attempts should be made on the plantations to improve the technical properties of raw rubber, especially from the point of view of variability in quality, by attempting to reproduce some of the conditions which are involved in the preparation of the *borracha fina* of Brazil. It is not a question of copying the method, or even certain phases of the method, employed in the Amazon region, but only of applying some modifications to the plantation methods in the light of Brazilian practice.

Fine para	Smoked sheet
(1) Coagulation hot.	(1) Coagulation in the cold.
(2) Coagulation brought by a number of substances, of which some have antiseptic properties.	(2) Coagulation by a single agent which has no antiseptic properties.
(3) Elimination of water by mild, continuous, progressive pressure.	(3) Elimination of water by sudden, short, more or less intermittent pressure.
(4) Material smoked during coagulation and before pressing.	(4) Material smoked after coagulation and pressing.

(1) In the Amazon process, the author has found that the smoke stream which impinges on the layer of latex to be coagulated has a temperature of at least 70° C. Tests were made with the bulb of a thermometer in the smoke at the point of contact with the latex film. The temperature of the rubber globules in the latex is, therefore, possibly somewhat lower.

(2) It is probable that the composition of the smoke varies within certain limits, but on the other hand it will have certain chemical and physical characteristics always the same. An insufficient number of chemical analyses have been carried out to determine this with certainty, but the *seringueiro* is able to recognize, by empirical methods, a smoke which is good for coagulation and one which is not.

(3) The Amazon rubber is prepared in the form of balls. The coagulum, which is at first quite plastic, gradually contracts and becomes more elastic in the course of time. A film coagulated on a given day contracts and in so doing adds a certain pressure to that exerted by the film coagulated on the previous day. On the following day a new film adds further pressure, and so on. The pressure on the mass thus rises slowly but progressively, since the latex is of one kind and the daily layers of rubber are of approximately equal thickness. In this respect the Brazilian method of preparation differs widely from that employed on the plantations.

(4) Smoking (in the Portuguese of Brazil *defumaçao*) is not to be compared with the smoke treatment of sheet rubber. In the Amazon process the smoke acts on the aqueous dispersion of rubber and not on the coagulated rubber, as in the preparation of smoked sheet, so that the whole mass of the rubber is thoroughly and simultaneously impregnated with the smoke before coagulation is complete. The smoke does not discolor the rubber, which remains creamy-white immediately after coagulation.

It is obvious that the Amazon *defumaçao* smoking process is uneconomical, and it could be applied on estates handling large quantities of latex only by the use of special machines. Many such machines have already been tried, but none has been found suitable in practice. It is certain, also, that it would be impracticable to prepare rubber in ball form, as this would involve an excessive time of drying, and could result in rubbers showing large variations in moisture content.

It is possible that insufficient attention has been given to an experiment which was carried out about 25 years ago in the higher reaches of the Amazon basin. Several thousand kilograms of rubber were prepared by the *defumaçao* method in the form of sheet. These sheets were submitted for examination to various manufacturers in Europe (in England, France, and Germany) and were considered superior to the usual ball form since buyers were prepared to offer a premium of about 14% for the material. This higher price corresponds approximately to the reduction in moisture content, which was brought down to the proportion usually found in plantation sheet rubber, and also, to a small extent, to a saving due to the reduction in the loss on washing. It seems, therefore, that rubber manufacturers considered this sheet otherwise equal in quality to ordinary fine Para. It is true that in those days people did not trouble themselves much about properties such as rate of vulcanization and aging resistance.

We believe that among the causes of variability of raw rubber the planter is unable to effect an improvement, as far as the qualities of the latex are concerned, except by the development of monoclonal plantations in which variations due to differences between individual trees are minimized. Since the majority of these causes are independent of the planter, variation in quality will persist.

On the other hand, we believe that it is possible to reduce the variability in quality by modifying the methods of preparation on the plantation if suitable economical processes can be found. It appears that these modifications should, by comparison with the Brazilian methods, be based on the choice of coagulant and on the pressure which is exerted on the coagulum; perhaps also on the temperature of coagulation and on the addition to the raw rubber of certain non-rubber substances derived from the latex.

A solution to this problem would be of importance both to the rubber manufacturer, whose work would be simplified, and to the planter, who could expect to obtain a higher price for his rubber. There is no question of obtaining complete uniformity in quality, but only of a reduction in the degree of variability, since there are a number of factors which are outside the control of the planter, at any rate from an economic point of view.

INFLUENCE ON FINAL PRODUCT OF FAST AND SLOW VULCANIZING RUBBERS *

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The object of this paper is to endeavor to carry beyond the laboratory stage the tests which have been hitherto published on the variability in vulcanization found in plantation rubber.

It is easily appreciated that, when one is handling large quantities of rubber, it is impossible for economic reasons to buy from one estate or even one group of estates, but the whole of the available rubber has to be surveyed before purchases can be made.

There are accepted classifications in London which, in many instances, are based on appearance rather than on intrinsic quality of the rubber. Cleanliness or eye value, although desirable, should not be the sole standard for quality of rubber.

Each broker, agent, dealer or middle man between producer and user has his own type sample. Each user has his own conception of what he wants and generally has a type sample also. But variation in available rubbers does influence the final product, especially in regard to the manner in which a rubber vulcanizes.

For the purpose of experiment, two wellknown rubber types have been chosen, and factory production runs covering a considerable tonnage have been studied.

Type 1. Smoked sheet tendered as No. 1 RSS London standard.

Type 2. Amber crepe, otherwise known as blanket crepe rubber.

Two lots of rubber were selected.

Code Mark:

DSS ...... A fully smoked dark sheet.
LSS .... A lightly smoked sheet but not air dried.
X;Y ...... Thick amber crepes.

The smoked sheet was tendered against RSS London Standard 1st quality contract, and the ambers tendered both as the same quality crepe rubber.

A considerable amount of rubber of each type was selected and masticated, both on open 84″ mills and in Banburys, using 300 lb. batches, and every effort was made to ensure that each batch was handled in exactly the same way. The rubber was divided into pieces of about the same size, two 84″ mills were selected, the nip set, and cooling water regulated to the same amount per mill. The rubber was fed into the mills at the same time, and the different portions of each were fed in the same sequence. Operators were changed over from one mill to the other after each batch. Automatic batch-cutting knives controlled the mastication. Simultaneously, on each mill, the same number of cuts was made from each side of the mill in the same sequence.

After the rubber had been milled for 20 minutes, it was batched off by rolling into 60-lb. rolls and allowed to remain until quite cool. This took several days. The mill roll temperatures during mastication were as nearly constant as it is possible to keep them.

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Rubber Industry, London, May 23-25, 1938. Paper No. 71, pages 370-380.

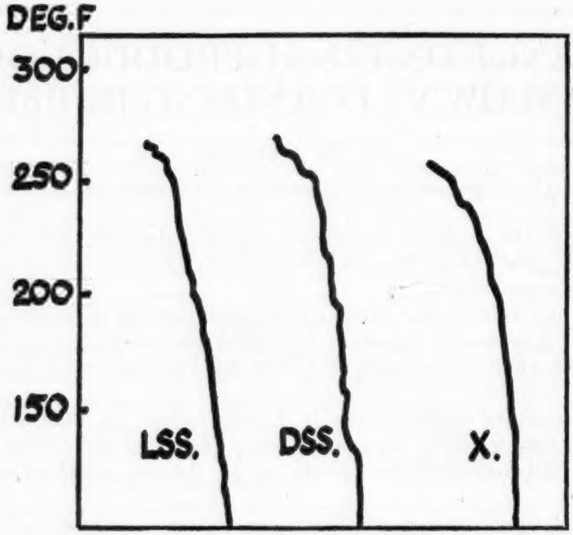

FIG. 1.—Temperature build-up, Banbury-masticated rubber, during first 12 minutes.

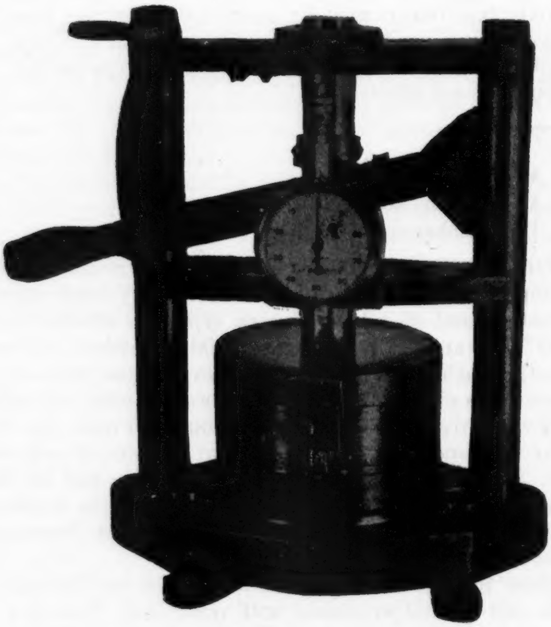

FIG. 2.—Williams' plastimeter.

In the case of Banbury masticated rubbers, four different Banburys were employed on a preliminary test run, and the one giving the lowest temperature at the end of masticating period was selected for the purpose of the experiment.

After the rubber had been masticated, it was passed through a sheeting mill, 3 samples taken, and the rubber rolled off and cooled in a manner similar to the rubber which had been mill masticated.

The object of using two methods of mastication was to cover the field generally employed in this country to masticate rubber and eliminate any advantage one method may have over the other.

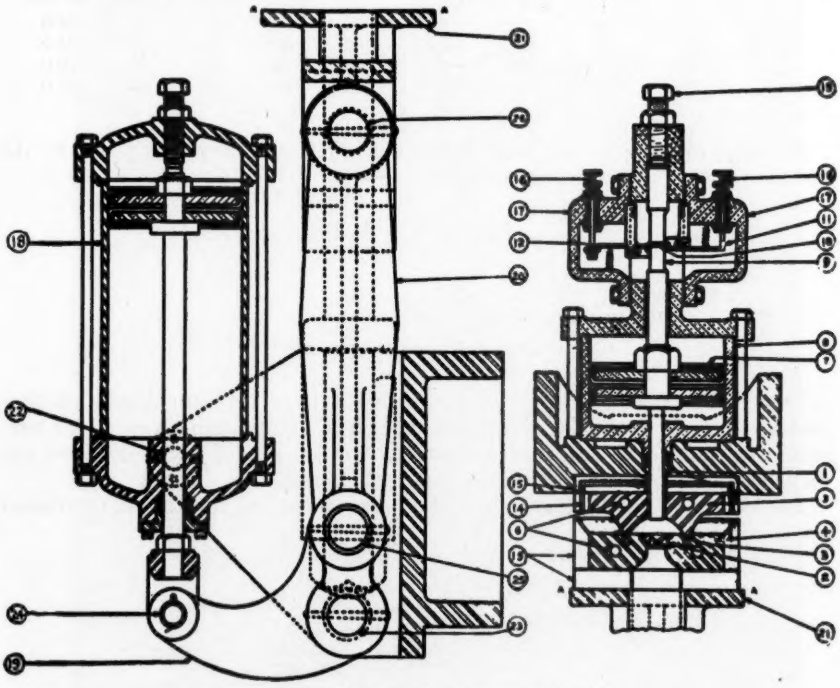

FIG. 3.—Simplified extrusion plastimeter (Dillon).

Figure 1 shows the actual temperatures obtained in the mass of rubber whilst in the Banbury. As was anticipated, the mill-massed rubber was considerably cooler.

Three samples were taken from each batch of rubber masticated, one sample from the rubber each side of the mill roll and one from the centre. They were cut 18 minutes after milling had started, and within the next two minutes the whole of the 300 pounds had been removed from the mill.

Each sample was divided into two parts.

The plasticity was taken in duplicate on each sample, using both the Williams plate-type and the Dillon-Johnson extrusion-type plastimeters. Both of these instruments were developed in the laboratories of the Firestone organization.

The average figures are given in Table 1, each group representing a considerable weight of rubber. The lower the figure, the softer is the rubber.

It will be seen that each roll of rubber whether cut from right, left or centre, was milled to the same degree of softness, and any difference which under other conditions could be attributed to variation in the masticating process may be considered eliminated.

TABLE I

PLASTICITY

	Mill masticated								Banbury-masticated Extrusion
	Williams				Extrusion				
	Left	Centre	Right	Average	Left	Centre	Right	Average	Average
LSS	4.30	4.30	4.10	4.20	70	70	70	70	91.0
DSS	4.20	4.41	4.10	4.17	50	50	50	50	44.0
X	4.10	4.20	4.00	4.10	40	40	40	40	29.0
Y	3.70	4.00	4.00	3.90	40	40	40	40	28.0

A composite sample was taken from each kind of rubber and mxied to the American Chemical Society formula.

Rubber	100.0	parts by weight.
Sulfur	3.5	" " "
Zinc oxide	6.0	" " "
Stearic acid	0.5	" " "
Mercaptobenzothiozole	0.5	" " "

Vulcanized, 60 minutes, at 260° F.

Twenty-four hours after vulcanization, slabs were cut into dumb-bell test-pieces and tested on a Scott testing machine. The results were corrected for temperature differences. To guard against jaw breaks, special jaws were used and the whole series of tests was made without jaw breaks.

The remainder of the tensile test-pieces were analyzed for free sulfur/rubber ratio.

The following results were obtained:

TABLE II

	Free S/R%	Modulus at 600%	Acetone Extract, %
DSS	1.50	910	5.10
LSS	1.65	930	3.25
X	1.40	760	3.55
Y	1.40	520	2.40

The production of each mill was stacked separately, but each lot of rubber was blended with itself, *i. e.*, the left, and right cuts as batched off from the mill were stacked alternately.

Each stack of each grade was blended with the other stacks of the same grade. By the employment of this method of handling it was felt that all batches of tread and body stock would be made with rubber the same in every way in so far as the preliminary mastication was concerned.

As to the ingredients in the stock under test, sufficient of each was isolated from current stock so there should be no need to get other supplies during the course of the investigation. Each ingredient was of standard commercial quality, and each was analyzed to the Firstone Company's particular specification.

In addition to chemical tests, the zinc oxide, carbon black, and mercaptobenzothiazole were compounded into rubber mixes. These mixes were vulcanized and physical tests done on the resultant stocks.

The results of the laboratory tests proved the ingredients to be up to specification in all respects, and no abnormalities were apparent.

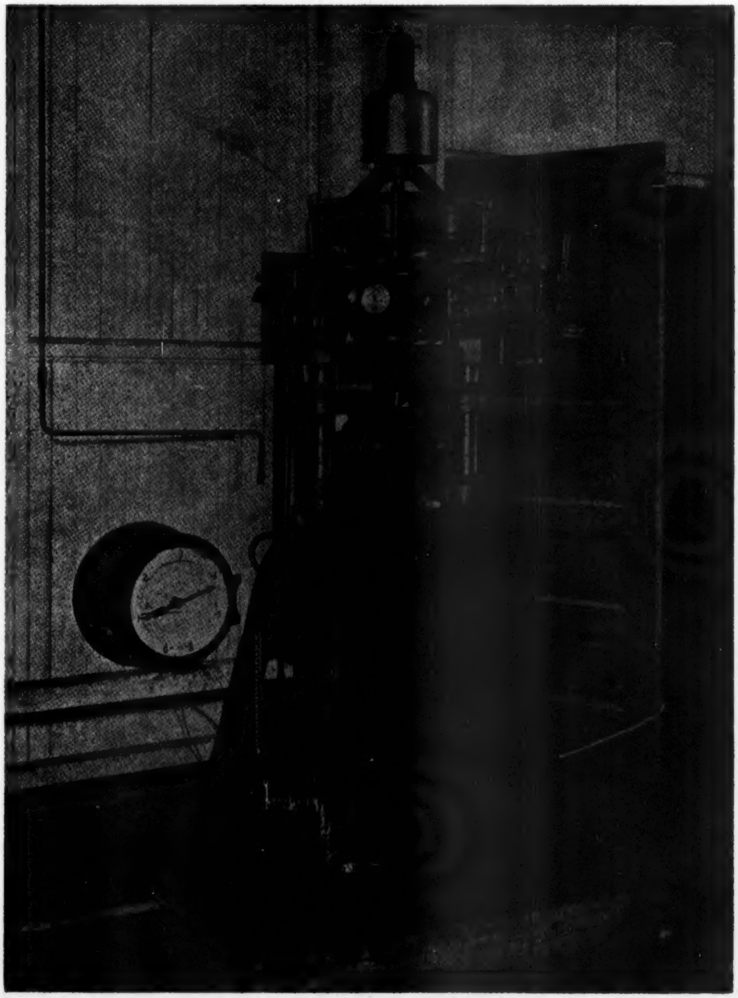

FIG. 4.—Dillon plastimeter.

The necessity of this testing of raw material was considered desirable, as with proved raw materials any variation in subsequent results could not be attributed to variation of compounding ingredients.

For the main investigation two types of stock were selected, a tread stock and a zinc compounded body stock, both accelerated with mercaptobenzothiazole.

The composition of the tread stock was:

Rubber	100.0 lbs.
Carbon black	57.0 "
Sulfur	3.0 "
Accelerator	1.0 "
Stearic acid	3.0 "
Pine tar	2.0 "
Antioxidant	1.0 "

The composition of body stock was:

Rubber	100.0 lbs.
Zinc oxide	46.0 "
Sulfur	4.0 "
Accelerator	1.0 "
Stearic acid	1.0 "
Pine tar	2.0 "
Antioxidant	1.0 "

Sufficient of each stock was mixed to ensure uninterrupted runs both on the tuber and calender.

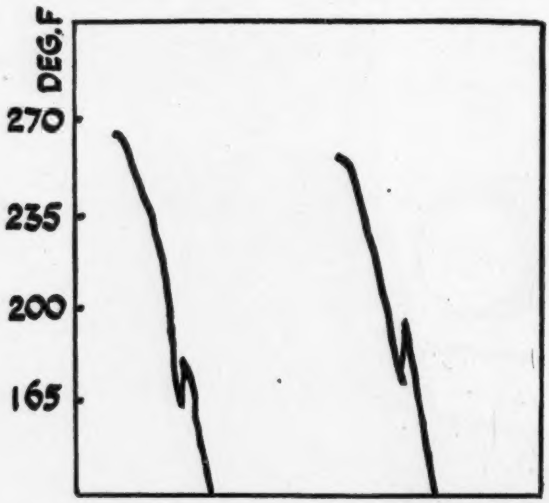

FIG. 5.—Temperature of mixed tread stock in Banbury.

The batches were compounded under close laboratory supervision, and the weights of individual materials checked on a special scale, which had been checked for accuracy before the compounding commenced. As a further check, the total weights of all materials used were again checked before issue to the mixing operators.

The rubber was used in such a manner that a blend of constant proportion of both mill and Banbury massed rubber was used in each individual batch of tread and body stock. The batches were mixed for the same total time in a Banbury, and care was exercised to see that the cooling of rotors, door and sides were regulated by using water of known temperature during each mixing.

A cooling period was allowed between batches to assure that the cooling surface of Banbury and mill were the same temperature at the commencement of each batch.

In Figure 5 are typical curves showing temperature of the stock while actually in the Banbury. They were obtained by means of thermocouples connected to thermometer recorders self-compensating for variation of cold-junction temperatures.

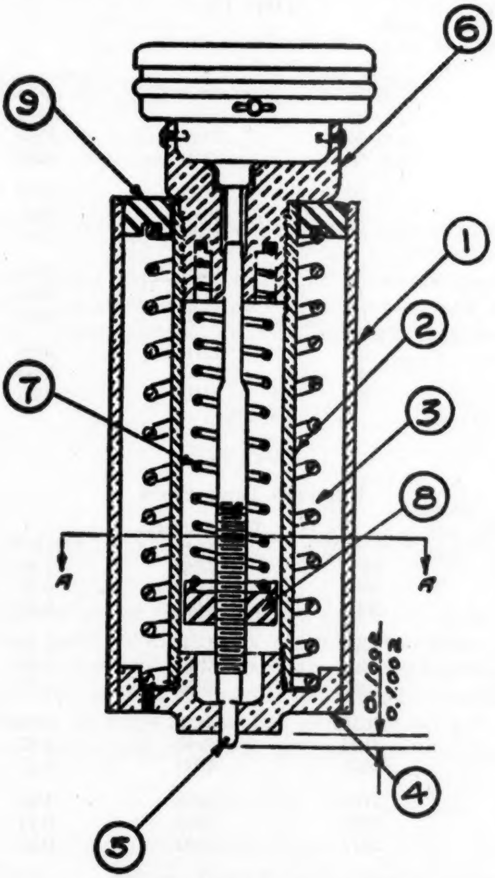

FIG. 6.—Cross section of penetrometer.

The sulfur was added on an 84″ mill and the period of mixing was closely controlled to get an even distribution of sulfur throughout the stock.

As a check on this, samples were cut from each side and from the centre of the stock and checked for specific gravity, vulcanization and sulfur.

The stock was cut off the mill in suitably sized slabs and water-cooled to air temperature, then stored for twenty-four hours before any further processing operation was done.

Mention should be made of the method adopted for hardness recording. The instrument used is known as the Firestone Penetrometer, and the index figure varies inversely as the hardness.

Varied load can be supplied by altering the springs which load the needle. The needle contact surface is a hemisphere of 3/32 inch diameter. Such an instrument is capable of more accurate reading than the Shore Durometer.

Samples of mill stock were taken, vulcanized in the laboratory and physically tested, with the following results:

TABLE III

MIXED TREAD STOCK

	Vulc., min. at 280° F.	Modulus 400%	Tensile strength, (lbs. per sq. in.)	Penetration
DSS	20	1560	3470	41
	40	2030	3980	33
	60	2170	3630	30
LSS	20	1170	3570	43
	40	1640	3920	35
	60	1790	3760	34
X	20	1440	2780	46
	40	2120	3630	39
	60	2000	3450	37
Y	20	1270	3060	51
	40	1980	3880	40
	60	2210	3950	33

TABLE IV

EXTRUDED TREAD STOCK

	Vulc., min. at 280° F.	Modulus 400%	Tensile strength, (lbs. per sq. in.)	Free S/R%	Penetration
DDS	20	1480	3380	1.48	44
	40	1800	3750	0.78	36
	60	2000	3450	0.42	35
LSS	20	1370	3310	1.76	44
	40	1600	3740	0.87	35
	60	1960	3850	0.57	33
X	20	1650	3420	1.62	46
	40	2190	3940	0.67	39
	60	2560	3700	0.37	37
Y	20	1750	3450	1.48	50
	40	2260	3850	0.71	42
	60	2370	3750	0.37	30

After taking a record of the plasticity of the batches, the tread stock was then blended by warming up on 4 mills, rolls off each mill were consequently blended and fed to feed mill. This blending was done to make sure that the treads extruded were truly respresentative of the stock mixed.

Knowing the plasticity, it was possible to set screw speed to extrude at an even flow and, owing to temperature recording devices and cooling water in machine walls, it was possible during the tubing, also to keep the whole of any particular stock at the same temperature.

It will be noticed that emphasis has been laid on temperature control throughout. The close control of all temperatures was to prevent any prevulcanization of the stock which would influence the final result.

The plasticities of the tread stocks were:

TABLE V

		Prior to extruding	Extruded treads
DSS	Extrusion	23.00	12.30
	Williams	4.10	3.50
LSS	Extrusion	18.15	11.00
	Williams	3.60	3.10
X	Extrusion	23.30	9.90
	Williams	3.70	3.20
Y	Extrusion	27.80	10.40
	Williams	3.60	3.00

The treads were cooled to air temperature, and six were selected to be built into tires.

The rubber used in tire body stock was a portion of the smoked rubbers previously mentioned. The stock was mixed on a Banbury and the same control exercised to see that batches were all treated alike as was exercised when the tread was being mixed.

TABLE VI

BODY STOCK

	Plasticity	
	Williams	Extrusion
DSS	2.30	21.0
LSS	2.40	29.0

The temperature curves for the batch show repetition of the cycle of mixing operation. For each batch sufficient stock was mixed to assure a production run, as only by such runs is it possible to prove in practice the laboratory experiments.

The work on the body stock was confined to testing the smoked sheet rubbers. Work is proceeding on the crepe rubbers but results are not yet available.

The samples were vulcanized at 280° F. and gave the following figures:

TABLE VII

CORD BODY STOCK

	Vulc., (min.)	Modulus (400%)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)	Free-sulfur rubber (%)	Penetration
DSS	20	1960	2650	660	1.33	89
	40	2200	2560	630	0.53	84
	60	2170	2500	620	0.14	83
LSS	20	1620	2300	670	1.81	97
	40	1620	2250	650	0.79	86
	60	1550	2430	600	0.33	86

Special tires were built from the above stocks. Each half tire contained stock wholly from the rubber under test. The parts were suitably identified.

All component parts of tires were specially selected to be the same dimensions, thus assuring even thickness throughout the tire.

The actual assembly was checked at all stages to be sure that no mixing of stocks took place.

Two complete 6 in. heavy-duty pattern tires were built and vulcanized at the same time. After vulcanization, the tire was cut in halves, each half being analyzed—all tests were made in duplicate. When one-half tire was completely tested, all remaining parts were collected and disposed of, thus guarding against possible errors in sampling.

Samples were cut from two portions of the tire tread, *viz.*, the surface at the maximum tire diameter designated as the tread crown, and the shoulder of the tire from that portion to the cushion breaker combination, designated as the tread base.

The rubber on the fabric plies was taken from the 4-5-6 plies which approximate the centre of fabric body.

Free sulfur was estimated in all samples, and in addition, tensile properties were determined on the treads.

The tires were vulcanized with water in the airbags and at low temperature, which is the general method of tire vulcanization.

It was arranged to vulcanize the tires in an autoclave. By so doing, it was possible to have the two tires under identical conditions, whereas in watch-case vulcanization, where only one tire can be vulcanized at a time, some error in operation may make duplication of vulcanizing conditions nearly impossible to obtain.

Vulcanization 55 min. at 258° F. and 90 min. at 280° F. on 320° F. water.

	Percentage free sulfur/rubber ratio			
	Crown	Base	Body plies	Body-ply adhesion
LSS	0.55	0.86	0.48	40 lb.
DSS	0.42	0.76	0.35	35 lb.
X	0.40	0.80	Not determined	—
Y	0.43	0.84	" "	—

The tensile properties of the tread were as follows. All results corrected for temperature variation, as in previous tests already noted.

	Modulus 400%
Crown DSS	1920
Base "	1800
Crown LSS	1900
Base "	1640
Crown X	2540
Base "	2360
Crown Y	2400
Base "	2250

It seems clear that this series of experiments has proved that the variation which is apparent in raw rubber is still apparent in the finished tire. There does not seem to be any previous published information which shows how the variation in raw rubber affects the final state of vulcanization in the finished product. One can easily see from the results obtained the necessity of testing all rubbers received, and of blending to obtain a uniform raw rubber with which to commence compounding.

Abrasion results on these rubbers show that some variation in abrasion was obtained, although no attempt has been made to find just which is the best state of vulcanization to give the least abrasion.

I should like to thank the Directors of the Firestone Organization for allowing the work to be done. Also, I wish to acknowledge the help given by the production side of the factory; the laboratory, particularly for the amounts of testing they have done to confirm results shown in the paper and the help given by the Anchor Chemical Co., Imperial Chemical Industries, Ltd. and Monsanto Co., in confirming some of the physical tests which have been made in our own laboratory. These check tests were made by outside firms with the idea of eliminating any variation which may be due to any one particular method of physical testing.

HIGH-SPEED APPARATUS FOR DETERMINATION OF PLASTICITY IN RUBBER WORKS AND SOME RESULTS *

J. HOEKSTRA

VENLO, HOLLAND [1]

Since the day that Hancock invented his wooden masticator, plasticizing has been one of the outstanding features of the rubber industry. Although the application of rubber in the form of latex, thus avoiding the process of mechanical softening, is increasing, this does not imply that the use of heavy machinery for plasticizing coagulated rubber is lessening.

It is now commonly accepted that plasticizing or mastication of rubber is a chemical process[2], occurring under combined mechanical and chemical (oxygen) influences and resulting in a diminishing of the length of the hydrocarbon molecules. This breakdown of rubber is of great technical importance, because the plasticity of rubber stock determines its workability. The degree of plasticizing or breakdown, especially when mastication has been prolonged, has also some effect on mechanical and aging properties after the plasticizing has been counterbalanced by the action of vulcanization.

It follows from the foregoing that control of plasticity during fabrication is of great interest from a technological standpoint. From the standpoint of works economy the problem is not less urgent, because energy used by internal mixers and mixing rollers as well as extra costs resulting from wrong plasticity in calendering and moulding are of importance in total production costs.

In recent years important contributions to the measurement of plasticity in general have come from rubber technologists[3, 4], and a good many instruments have been described. Without giving a general review of the work done on the subject, mention may be made of the plastimeters of Williams[5], of Marzetti[6] and of Mooney[7]; these are prototypes of plastimeters now in use in the rubber industry. There are many variations of these three types: compression, extrusion and shearing plastimeters[8-16].

The purpose of the work undertaken by the author was to find a way to measure plasticity of rubber stock taking very little time. The time needed for preparation of sample and complete measurement was to be so short that a rubber stock which was being worked on a factory or laboratory mill would not change appreciably in plasticity during this time. A maximum of 1½ minutes was fixed for the purpose.

More than one plastimeter has already been constructed with a view to shortening the time needed for a determination.

Of these the extrusion method of Behre[15] requires a separate determination of the temperature; moreover, it is said to be necessary to take the average of a number of measurements to obtain true results. It therefore seems improbable that this method is quick enough for the purpose mentioned.

Moreover, the author is of opinion that in general extrusion and also pure shearing are mechanically rather difficult to realize. Compression between parallel plates, though in its mechanism by no means simple, is much easier to realize.

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 63, pages 362-368.

The compression plastimeters of Usherwood[12], Karrer[9] and the Scott Company[11] all use short compression times, but the specimen has to be warmed beforehand, which takes more time. The Scott plastimeter has its plates warmed by steam, and warming of the samples is done in the plastimeter itself. This method was used also by the author (whose plastimeter was designed without knowledge and before publication of the Scott plastimeter).

The limited time of one and one-half minutes allowed for one determination necessitated the use of very thin rubber specimens, for pieces of rubber that are thicker than 1 mm. require too much time to attain a uniform temperature.

Preforming and heating of the specimen is done between the steam-heated dies of the plastimeter itself.

It proved necessary to wrap the sample of plasticized rubber or rubber mixture in a piece of paper, *e. g.*, cigarette paper. The slipping of unvulcanized rubber stock along dies of steel or copper is so pronounced at a temperature of 100° C. and a pressure of 10 kg. per sq. cm., as used in the plastimeter to be described, that it was impossible to check plasticity values without the use of paper. This phenomenon of slipping has its disturbing effect on the mechanism of compression only during the first seconds after the pressure is applied. Therefore with compression plastimeters like that of Williams, as modified by van Rossem and van der Meijden[8], or of Hoekstra[10] the slipping has not as yet been found to be troublesome for plasticized stock (see, however, T. L. Garner[17]).

In practice it was found that the preparation of samples for the short-time plastimeter from a sheet of rubber which is being worked on the rolls takes more time than the determination itself. Therefore a special strong rubber punch in the form of a pair of tongs was constructed. This apparatus is constructed in such a way as to punch samples of nearly the same volume out of heavy sheets of plasticized rubber or of rubber mixtures varying much in thickness.

As the short-time plastimeter has to be handled in the rubber factory, the instrument must not be too heavy and must be very sturdy. Therefore weights were not taken as the source of pressure, but a pair of coiled steel springs.

The plastimeter built according to the principles which have just been mentioned, will now be described in some detail (see Fig. 1)[18].

A pair of iron jaws 10 and 11 (detail A and B), with their fulcrum axis at the left end, each carry at their right end a copper bar. Compression is effected between the flattened ends of these bars. The system so far is the same as that of the author's balance-plastimeter[10]. The upper end of the lower bar has a surface of 1 sq. cm. The under surface of the upper bar is a little larger, so that compression is effected in the way indicated by van Rossem[8], the sample being compressed by means of a constant force per square centimeter.

Both jaws carry a yoke, at both ends of which the two springs, 13, are fastened. The two springs are stretched to the desired stress (10 kg.) by means of a screw-nut.

The copper bars are surrounded by double copper half-spheres, as shown in Figure 1, detail D. In this way a small spherical cell is formed round the ends of the copper dies when the jaws are in a closed position. Steam, circulating between the double walls of this sphere and through holes in the bars, maintains a constant temperature.

The relative displacement of the dies towards each other is magnified some 100 times by a very simple system of needles, 3 and 4, and read on an adjustable scale, 8. This thickness gauge comes into action only when the rubber sample is compressed to 1 mm.

The jaws are opened and let loose by means of a lever, 7; when this lever is moved to the left, the specimen can be easily put between the jaws; in the middle position, the sample is compressed to 1 mm. and warmed; when the lever is moved to the right, the springs are set free and the sample is compressed with a force of 10 kg. The stress of the springs 13 is calibrated by means of a loose iron yoke 12, which lengthens the upper jaw 10, to the left. A weight of 10 kg. is hung at the

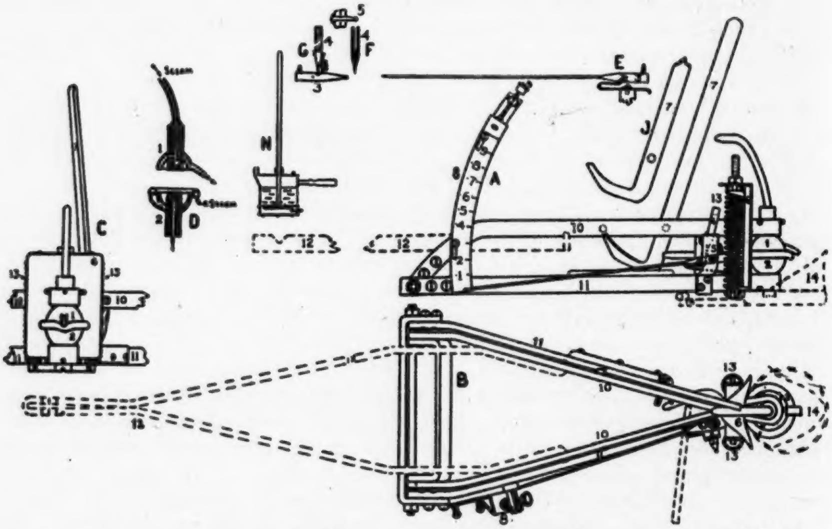

FIG. 1.—Short-time plastimeter. A, side view; B, plan; C, front view; D, steam-heated press bars; E, F, G, thickness measuring device; J, lever; N, steam supply.

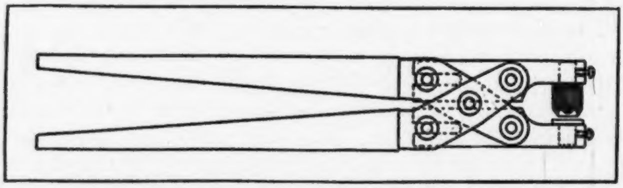

FIG. 2.—Punch for cutting samples from plasticised sheet. Side view (die in cross-section). Diameter of cutting die, 12 mm.

left end of this yoke and the springs are tightened or loosened till the jaws are just opening.

Figure 2 shows the rubber punch. This punch compresses and cuts at the same time; with heavily-loaded tread stock the pressure needed is rather considerable.

As the apparatus was designed solely for technical ends, no provision was made for obtaining compression or shearing curves, but only a single, arbitrarily fixed, compression datum from each test.

Many determinations were made with the instrument on raw sheet and crepe, plasticized from 2 to 20 minutes on laboratory rolls. It was found that a preforming (and warming) time of only 5 seconds was sufficient; it made no difference to the reproducibility of results whether a time of compression of 15 or of 30 seconds

was taken, so that the former was chosen. It was found that the average deviation of the values from their average was 2%.

The short-time plastimeter does not give the same plasticity values as the de Vries-van Rossem and balance plastimeters (these latter do agree)[10]. As both compressing force and temperature are different, no proportionality between the two ways of determining plasticity is to be expected.

	Compressive force	Compress surface	Time of compression usually	Temperature
de Vries-von Rossem plastimeter......	5 kg.	1 sq. cm.	10 min.	70° C.
Short-time plastimeter	10 kg.	1 sq. cm.	¼ min.	100° C.

Comparison of the balance and the short-time plastimeters with many different rubber stocks gave the relation shown in Figure 3. The stocks used were: F. L. crepe and sheet, and mixings with 20% by volume of carbon black, zinc oxide,

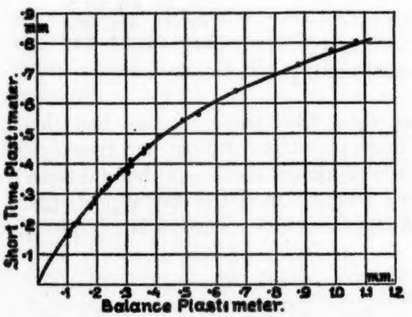

FIG. 3.—Comparison of short-time and balance plastimeters with various stocks.
Balance Pl.:—10 min. compression, 5 kg. per sq. cm., 70° C.
• Short-Time Pl.:—15 sec. compression 10 kg. per sq. cm., 100° C.

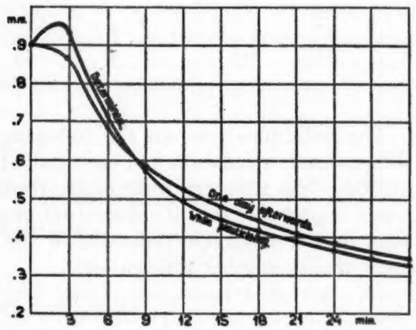

FIG. 4.—Plasticizing of F.L. crepe on laboratory rolls. Change in plasticity while rubber is on the rolls and one day later.

talc, natural and precipitated calcium carbonate and barium sulfate, and a few other ingredients.

It is seen that all the results lie on one line. So it may be concluded that the same rheologic property of rubber stocks is measured with the common compression plastimeters and the short-time plastimeter.

Having now described the short-time plastimeter and its mode of use, and having given a comparison of its values with those of a well-known compression plastimeter, some applications of the instrument will be described.

In the first place the instrument can be used in plasticizing rubber stock to a predetermined value. Working with rolls of dimensions common in rubber works, the experimenter has ample time for his determinations. Mastication can be stopped at any plasticity value wanted, as soon as the stock has been worked to homogeneous consistency.

With smaller laboratory rolls, where plasticizing progresses more quickly than on factory rolls, the author found it almost as easy to plasticize to a predetermined plasticity number.

An example, showing also some peculiar features, is given in Table I and Figure 4.

It is remarkable that the stiffness of the crepe increases during the first minutes on the rolls (before a smooth sheet has formed on the front roll). This phenomenon was always found. The effect must be ascribed to stresses set up in the raw crepe by the first passes through the rolls (not unlike strain-hardening in metals).

TABLE I

PLASTICIZING OF F. L. CREPE ON LABORATORY ROLLS

Time of plastizing	Immediate determination	Determination after 1 day
0 min.	90, 87, 87, 91, 91	—
3 "	93, 96	85½, 83, 89, 90
6 "	73, 77	70½, 68, 69½, 68½
9 "	57, 56	60, 58, 59, 57½
12 "	49½, 49	53, 54, 52, 53½
15 "	45, 46	49, 48, 46, 48
18 "	40½, 42	43½, 44½, 44, 44
21 "	40, 38½	41, 40½, 40, 40
24 "	37, 38	38, 38, 39, 37
27 "	35, 35	36, 38, 37½, 36½
30 "	32½, 33	34½, 34, 35, 34½

Temperature of roll surface was kept at 50° C.

The determinations on the following day show that these stresses had then disappeared; relaxation had occurred. The more plasticized rubber had recovered a little. This recovery from mastication is a well-known fact in rubber factories, but it is probable that it shows itself more in a restoration of the elastic properties than in a considerable reduction of the rheologic mobility. The author hopes to show this in another publication.

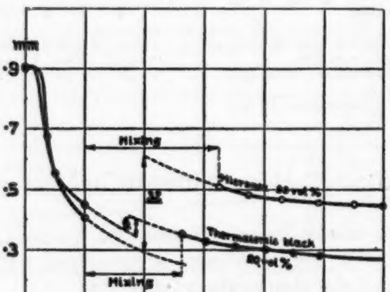

FIG. 5.—"Stiffening value" of two types of carbon black, by means of plasticity-time curves of "pure gum" and mixed stocks.

A second example of the use of the instrument is the determination of the stiffening action of pigments. During the mixing of rubber and pigment, plasticizing goes on. Therefore the best method to determine the "stiffening value" of a pigment seems to be to follow the whole process with the short-time plastimeter. The plasticity-time curves for "pure gum" and for mixed stock are then extrapolated. As the plasticity-time curves of different rubber stocks (worked on the same rolls and in the same way) prove to be almost parallel, extrapolation can be done with the help of a plasticity-time curve for "pure gum."

The difference in plasticity between the two curves for gum and stock is taken as the stiffening value of the pigment. The method has no great exactness, but is useful for the purpose.

An example is given in Figure 5, where the very pronounced difference in stiffening action between two types of carbon black is demonstrated. The curves given were found with 20 vol.-% of pigment; the stiffening action was found to be directly proportional to the volume concentration of pigment.

Full details of these determinations of "stiffening values" will be published elsewhere.

"Scorching" effect can be followed on laboratory rolls with the instrument. Stiffening is seen on the rolls initially as a contraction on the surface of the rubber stock, at the same time as it is read from the plasticity curve as an augmentation of stiffness from 0.14 to 0.21. The use of the instrument for the prevention of scorching on factory rolls has not been tried out by the author.

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